THE JOURNAL OF THE AMERICAN CERAMIC SOCIETY, JULY 1, 1944

Vol. 27, No. 7, pp. 197-220 (1944)

THE JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

AUGUST 1, 1944

MONTHLY PUBLICATION DEVOTED TO THE ARTS AND SCIENCES RELATED TO THE SILICATE INDUSTRIES

TABLE OF CONTENTS

Vol. 27 August 1, 1944 No. 8

THE JOURNAL

Effect of Substituting MgO for CaO on Properties of Typical Soda-Lime Glass 221–25
By Owens-Illinois General Research Laboratory

Melting Rate of Soda-Lime Glasses as Influenced by Grain Sizes of Raw Materials and by Additions of Cullet 225–31
By J. C. Potts, George Brookover, and O. G. Burch

Suggestions for Solution of Difficult Glaze-Fit Problem 231–33
By C. G. Harman

Strontia and Its Properties in Glazes 233–38
By Earl S. McCutchen

Some Factors Affecting the Pyrometric Cone Equivalent of Silica Fire Clay 239–41
By Raymond E. Birch and M. P. Hall

Lightweight Superduty Kyanite-Topaz Refractory 241–46
By W. W. Galbreath, Jr., T. N. McVay, and Dan Allen

High-Alumina Clays of Pulaski and Saline Counties, Arkansas 246–49
By Joshua I. Tracey, Jr.

Publication Office: 20th & Northampton Sts., Easton, Pa.
Editorial Office: 2525 N. High St., Columbus 2, Ohio
Committee on Publications: R. L. Stone, *Chairman;* R. E. Birch, H. Z. Schofield, H. Thiemecke, and R. C. Purdy, *ex officio*

Entered as second-class matter at the post office at Easton, Pa., under the act of March 3, 1879. Published monthly
Subscription fifteen dollars ($15.00) a year. Single numbers $1.50
(Foreign and Canadian postage, 50¢ additional on subscriptions)
(Copyright 1944, American Ceramic Society, Inc.)

THE JOURNAL
OF
THE AMERICAN CERAMIC SOCIETY

Volume 27 August 1, 1944 Number 8

EFFECT OF SUBSTITUTING MgO FOR CaO ON PROPERTIES OF TYPICAL SODA-LIME GLASSES *

By Owens-Illinois Glass Company General Research Laboratory

Abstract

In base glasses containing (*a*) Na_2O 16, CaO 10, and SiO_2 74% and (*b*) Na_2O 14, CaO 12, and SiO_2 74%, MgO was substituted in steps of 2% for CaO. The effects of the substitution on liquidus temperature, viscosity, fiber softening point, and the resistance of the glasses to dilute acid and to distilled water are described.

I. Introduction

This laboratory, during the past several years, has carried out a number of investigations on the effect of composition on several physical and chemical properties of that type of glass commonly referred to as "soda lime." Two of the largest series studied have been (*a*) the system Na_2O–CaO·MgO–Al_2O_3–SiO_2 and (*b*) the system Na_2O–CaO–Al_2O_3–SiO_2. Several of these studies have been described.[1]

The present study describes some of the results obtained when CaO is replaced by MgO in two typical soda-lime-silica glasses. The effect of MgO is important in the glass industry because of the widespread use of dolomitic lime both with and without calcite lime.

II. Chemical Composition and Preparation of Glasses

The raw materials used in the preparation of the glasses were Ottawa sand, Solvay soda ash, burned lime, calcined magnesite, and ammonium sulfate. Ammonium sulfate, in an amount sufficient to yield approximately 0.2% of SO_3 in the finished glass, was used as a refining agent in the preparation of all glasses.

Approximately 4.5 lb. of each glass were melted in a large covered platinum crucible in a gas-fired furnace. The glasses were stirred several times during the initial melting period and were poured, crushed, and remelted, with additional stirring. The total time of melting and remelting was approximately 20 hours at 2600°F.

The actual chemical analyses as well as all measured properties of the 10%-lime glasses and 12%-lime glasses are shown in Table I. Glass No. 1 and glass No. 7 is the base glass, respectively, for the 10% and 12% series.

III. Properties Measured and Methods of Determination

The properties of the glasses determined were (1) liquidus temperature, (2) viscosity, (3) resistance to dilute acid, and (4) resistance to distilled water. The methods of determination were exactly the same as those previously reported in this work[1(d)] except for resistance to distilled water.

The previously described method worked well for compositions ranging from pure CaO glasses to those with a MgO content just beyond that for dolomitic-lime glasses. The direct titration of the 40-ml. aliquot gave increasingly vague end points with methyl red for compositions approaching pure MgO glasses. A definite amount of standard acid, added to these solutions and boiled briefly, was approximately neu-

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, April 5, 1944 (Glass Division). Received April 5, 1944.

This work has been a cooperative effort under the supervision of C. L. Babcock. The following members of the research staff were responsible for the preparation of the glasses, chemical analyses, and measurements of the various properties: J. C. Coleman, J. Miller, Paul Close, W. B. Silverman, H. H. Holscher, and F. R. Bacon.

[1] (*a*) W. B. Silverman, "Effect of Alumina on Devitrification of Soda-Lime-Silica Glasses," *Jour. Amer. Ceram. Soc.*, **22** [11] 378–84 (1939).

(*b*) W. B. Silverman, "Effect of Alumina on Expansion and Deformation Temperatures of Soda-Lime-Silica Glasses," *Jour. Soc. Glass Tech.*, **24** [102] 59–72 (1940); *Ceram. Abs.*, **19** [10] 232–33 (1940).

(*c*) W. B. Silverman, "Effect of Alumina on Devitrification of Sodium Oxide-Dolomite Lime-Silica Glasses," *Jour. Amer. Ceram. Soc.*, **23** [9] 274–81 (1940).

(*d*) Owens-Illinois Glass Company General Research Laboratory, "Effect of Barium Oxide and Zinc Oxide on Properties of Soda-Dolomite Lime-Silica Glass," *ibid.*, **25** [Feb. 1, No. 3] 61–68 (1942).

(*e*) Owens-Illinois Glass Company General Research Laboratory, "Effect of Iron Oxide on Properties of Soda-Dolomite Lime-Silica Glass," *ibid.*, **25** [Oct. 1, No. 14] 401–408 (1942).

TABLE I

EFFECT OF REPLACING LIME BY MAGNESIA ON PHYSICAL PROPERTIES OF 10%- AND 12%-LIME BASE GLASSES

	10%-CaO base glass						12%-CaO base glass						
Glass No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Composition	Composition (%)												
SiO_2	73.5	73.7	73.9	73.7	73.3	73.5	73.2	73 6	73.6	73.4	73.8	73.6	73.4
Al_2O_3	0.3	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2
CaO	10.0	8.1	6.1	4.1	2.4	0.3	12.2	10.1	8.2	6.3	4.3	2.3	.3
MgO	0.2	2.0	4.0	6.0	8.0	9.9	0.1	2.0	4.0	5.9	7.8	10.0	11.9
Na_2O	15.8	15.7	15.6	15.7	15.8	15.9	13.8	13.8	13.6	13.8	13.8	13.8	13.8
	99.8	99.7	99.8	99.7	99.7	99.8	99.6	99.7	99.6	99.6	99.9	99.9	99.6
	Chemical resistance with respect to H_2O and H_2SO_4												
Na_2O (%) in H_2O	0.062	0.069	0.070	0.072	0.060	0.048	0.036	0.043	0.050	0.055	0.056	0.049	0.033
Na_2O (%) in H_2SO_4	0.070	0.062	0.058	0.051	0.047	0.049	0.032	0.033	0.027	0.025	0.022	0.023	0.022
	Liquidus (°F.) and primary phase												
	1840 T*	1825 T*	1775 T*	1690 T*	1670 D†	1885 P‡	1960 T*	1895 T*	1800 T*	1835 D†	1890 D†	1975 P‡	2090 P‡
Log-viscosity	Viscosity-temperature relation (°F.)												
7.65	1305	1301	1299	1310	1330	1360	1342	1330	1335	1346	1359	1382	1398
7.00	1365	1365	1360	1375	1395	1425	1400	1390	1400	1410	1425	1450	1465
6 00	1475	1480	1480	1500	1510	1550	1510	1505	1515	1530	1545	1570	1585
5.00	1620	1635	1635	1665	1665	1710	1660	1650	1670	1690	1700	1735	1745
4.00	1820	1845	1850	1885	1885	1935	1860	1850	1875	1910	1920	1955	1960
3.00	2105	2150	2160	2205	2215	2255	2150	2140	2170	2215	2235	2270	2260
2.00	2550	2625	2655	2710	2780	2770	2610	2585	2610	2690	2720	2765	2710

* T, tridymite phase; † D, diopside phase; ‡ P, phase 1.

tralized regardless of its amount (within an upper limit).

This behavior may have been the result of (*a*) the solution of alkaline constituents in suspended solids carried over by the pipette or (*b*) hydrolysis of a dissolved silicate (probably containing magnesium) with resulting increase in the alkalinity of the solution. Either of these processes occurring slowly at the methyl red end point and rapidly in boiling acid could have caused the observed effect. Filtration of the solution resulting from a test through fine-textured paper (Whatman No. 42) failed to affect the behavior, indicating that the material was very fine, if undissolved.

Boiling the solution resulting from the test with a very large excess of acid produced a solution which gave a sharp end point with methyl red when titrated in either direction. This procedure had apparently driven the interfering reaction to completion. The fact that a sharp end point was finally reached indicated that the difficulty was not the result of the dissociation behavior of dissolved magnesium hydroxide.

The regular method calls for boiling the acidified extract to eliminate carbon dioxide. Back titration then gives a sharper end point than is obtained by direct titration. The effect of carbon dioxide, however, at the hydrogen-ion concentration of the methyl-red color change is so small that approximately the same result is reached. The data given on the resistance to distilled water have been based on a rapid direct titration of the 40-ml. aliquot. This method applies to all glasses having MgO contents beyond the percentage found in dolomitic lime. It is believed that the uncertainty of the data increases as the pure MgO glasses are approached.

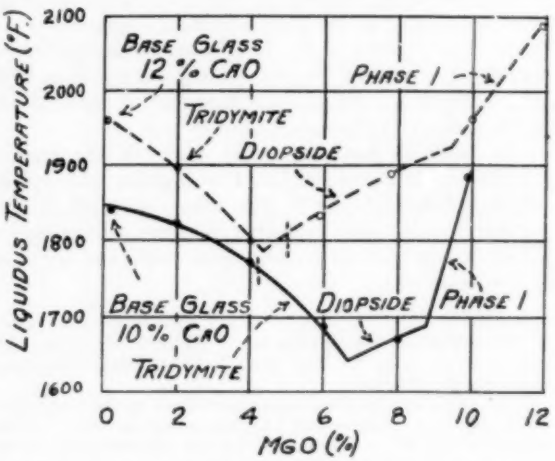


FIG. 1.—Effect of MgO substitutions for CaO on liquidus temperature.

IV. Discussion of Results

The measured data on the thirteen glasses are given in Table I, and Figs. 1 to 5 show in graphical form the effect of the substitutions on the various properties.

(1) Liquidus Temperature

The only study on mixed CaO and MgO glasses is that of Morey,[2] who gave data on nine glasses in the system Na_2O–CaO–MgO–SiO_2. This work showed

[2] G. W. Morey, "Effect of Magnesia on Devitrification of Soda-Lime-Silica Glass," *Jour. Amer. Ceram. Soc.*, **13** [10] 714–17 (1930).

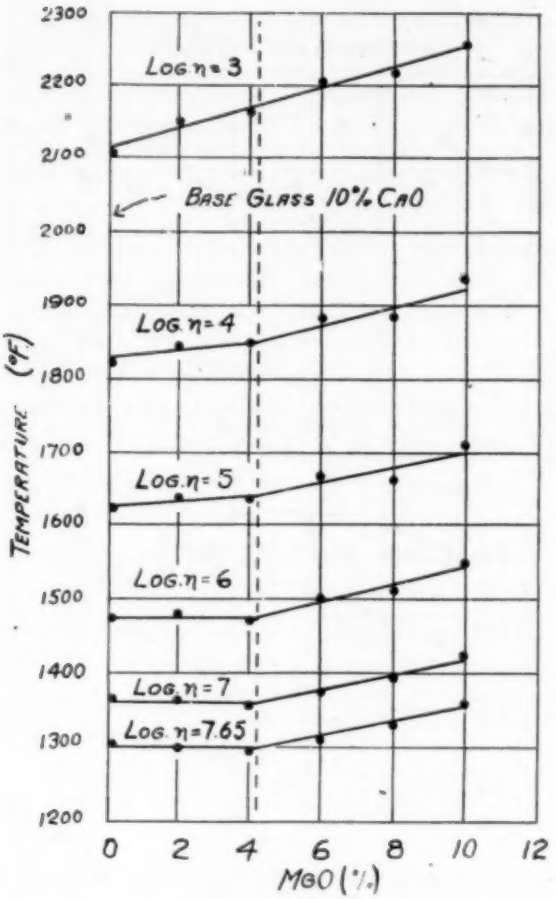


FIG. 2.—Effect of MgO substitutions for CaO on viscosity (10%-lime glasses).

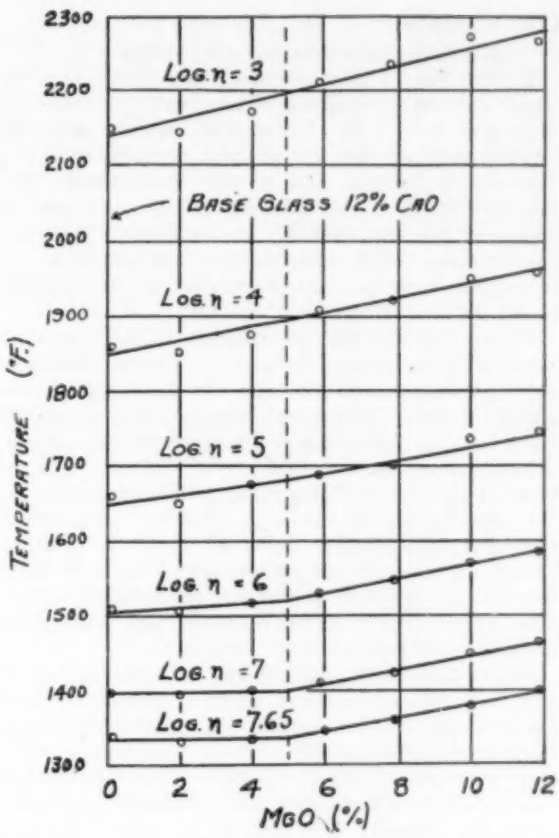


FIG. 3.—Effect of MgO substitutions on viscosity (12%-lime glasses).

that a remarkable lowering of the liquidus tempera ture resulted when MgO replaced CaO in certain compositions. His study also indicated that certain glasses made from mixtures of the two kinds of lime would have liquidus temperatures lower than those made using either one exclusively.

The present study adds a few more data to the Na_2O–CaO–MgO–SiO_2 system.

Figure 1 shows the effect on the liquidus temperature caused by substituting MgO for CaO in the two series of glasses.

The replacement of CaO by MgO in the 10%-lime glasses lowers the liquidus temperatures continuously until almost 7% of the CaO has been replaced by MgO, which is well beyond the dolomitic-lime ratio. All of these glasses are in the tridymite field. Further substitution of MgO for CaO causes a slight increase in liquidus temperature up to about 9% MgO. These glasses have diopside as primary phase. Further replacement causes a very rapid rise in liquidus temperature, the 10%-MgO glass being higher than the 10%-CaO glass. The composition of this phase is unknown, and for this reason it is referred to merely as phase 1.

It should be pointed out that the shapes of the curves for these two series of glasses are not drawn in an arbitrary manner. The phase boundaries have been determined by blending the composition shown to yield intermediate glasses for liquidus determinations.

The replacement of CaO by MgO in the 12%-lime glasses lowers the liquidus temperatures for the MgO contents up to about 4.4%. The MgO content for the dolomite lime glass is 5%. These glasses have tridymite as primary phase. Further substitution of MgO for CaO causes a continuous increase until about 9.5% MgO content is reached, these glasses having diopside as primary phase.

Further replacement causes a rapid rise in liquidus temperature, the 12%-MgO glass being much higher than the 12%-CaO glass; these glasses have phase 1 as the primary phase.

The data for both series show that glasses containing CaO and MgO in the dolomitic-lime ratio have lower liquidus temperatures than the respective glasses containing no MgO.

The data for both series show that the total replacement of CaO by MgO results in an increase in liquidus temperature, the increase being greater in the 12%-lime glasses.

(2) Viscosity

Complete viscosity data are given in Table I.

Figures 2 and 3 show the effects of replacing CaO by MgO on the temperatures necessary to attain log viscosities 3 to 7.65. These data will be discussed on the basis of viscosity at high temperatures (log viscosity = 3) and also at low temperatures (log viscosity = 6). The curves shown are considered to represent the data in the best manner. The discussion given here is based on that representation. It is realized, however, that the reader may wish to represent the data in a different manner.

Figure 2 shows that substitution of MgO for CaO in the 10%-lime glasses causes a continuous increase in the high-temperature viscosity throughout the composition range. This substitution has no appreciable effect on the low-temperature viscosity up to the dolomitic-lime ratio at 4.2% MgO. Further replacement of CaO by MgO results in a definite increase in the low-temperature viscosity. The low-temperature viscosity data indicate definitely that the rates of change in viscosity per percent substitution of MgO for CaO are different for the two composition ranges. The difference in character between these two regions decreases as the temperature increases.

Figure 3 shows that substitution of MgO for CaO in 12%-lime glasses produces changes similar to those found in the 10%-lime glasses. The high-temperature viscosity increases continuously in going from a 12%-CaO glass to a 12%-MgO glass. This substitution has little or no effect on the low-temperature viscosity up to the dolomitic-lime ratio at 5% MgO. Further replacement of CaO by MgO, beyond the dolomitic-lime ratio, results in a definite increase in the low-temperature viscosity.

The changes produced in the high-temperature viscosity by the replacement of CaO by MgO are approximately the same for both the 10%- and 12%-lime glasses.

The changes produced in the low-temperature viscosity by this substitution are similar for both the 10%- and 12%-lime glasses. Little or no change occurs up to the respective dolomitic-lime ratios for the two series. Further substitutions, however, beyond the respective dolomitic-lime ratios raise the low-temperature viscosity some 10°F. per percent for both series.

(3) Resistance to Dilute Acid

The effect of the substitution of MgO for CaO on resistance to dilute acid for both series is shown in Fig. 4. This substitution causes an appreciable improvement in both the 10%- and 12%-lime glasses. This improvement appears to decrease in degree as MgO is increased beyond that of the dolomite ratio.

(4) Resistance to Distilled Water

Figure 5 shows the effect of replacing CaO by MgO on water resistance for both the 10%- and 12%-lime glasses.

The water resistance decreases moderately as MgO replaces CaO in the 10%-lime glasses until the MgO content is near the dolomitic-lime ratio at 4.2% MgO. Further substitution results in a definite improvement in water resistance, the 10%-MgO glass being more resistant than the 10%-CaO glass.

The water resistance decreases substantially as MgO replaces CaO in the 12%-lime glasses until the MgO content is beyond the dolomitic ratio of 5% MgO. Further substitution results in a definite improvement in water resistance, the 12%-MgO glass being approximately the same as the 12%-CaO glass.

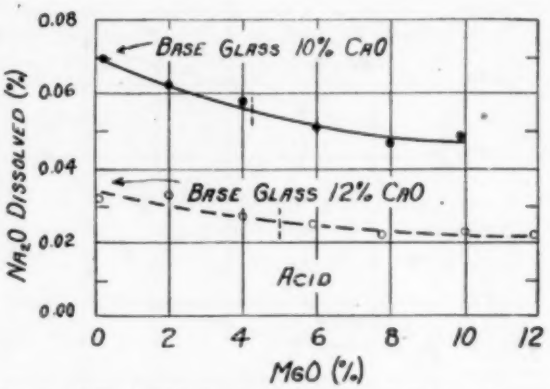


FIG. 4.—Effect of MgO substitutions for CaO on resistance to dilute acid.

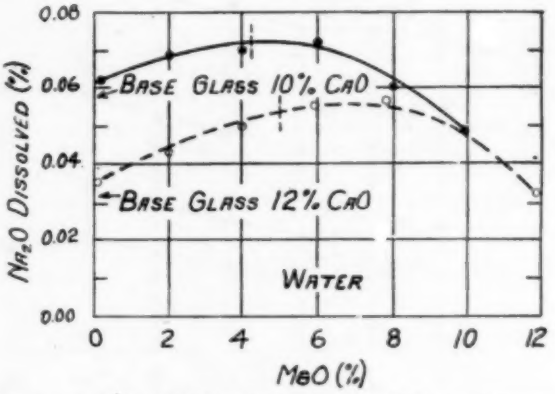


FIG. 5.—Effect of MgO substitutions for CaO on resistance to distilled water.

V. Conclusions

The following conclusions and observations may be drawn from the data presented on the substitution of MgO for CaO in the two base glasses.

(1) The substitution of MgO for CaO in both the 10%- and 12%-CaO glasses causes at first a lowering of the liquidus temperature and then an increase. The minimum liquidus temperature in the 10%-lime glass occurs at nearly 7% MgO, whereas the minimum occurs in the 12%-lime glass near 4.4% MgO. The liquidus temperatures of the dolomitic-lime glasses are lower than the respective calcite-lime glasses in both series. The glasses in which MgO has completely replaced CaO have higher liquidus temperatures than the respective CaO glasses in both series.

(2) The replacement of CaO by MgO results in an increase of viscosity at high temperatures for both series of glasses throughout the respective composition range. This substitution produces little or no effect on the low-temperature viscosity for compositions up to the dolomitic-lime ratio, but a definite increase in viscosity occurs in compositions having a higher MgO content. This is true for both the 10%- and 12%-lime glasses.

(3) The substitution of MgO for CaO causes a continuous improvement in the resistance to dilute acid in both the 10%- and 12%-lime glasses.

(4) The replacement of CaO by MgO in the 10%-lime glass causes a moderate decrease in resistance to distilled water for compositions up to the dolomitic-lime ratio, further substitution of MgO for CaO results in a definite improvement.

The replacement of CaO by MgO in the 12%-CaO glass causes a definite decrease in resistance to distilled water for compositions up to and beyond the dolomitic-lime ratio; in further substitutions of MgO for CaO, a definite improvement occurs.

Owens-Illinois Glass Company
General Research Laboratory
Toledo, Ohio

MELTING RATE OF SODA-LIME GLASSES AS INFLUENCED BY GRAIN SIZES OF RAW MATERIALS AND ADDITIONS OF CULLET*

By J. C. Potts, George Brookover, and O. G. Burch

Abstract

Using the complete solution of silica grains as a criterion of melting, a comparison of the melting rate of a typical soda-lime glass as affected by the grain size of the constituent materials has been made. This study indicates that if the grain sizes of raw materials are mismatched, separation or demixing of the batch during melting is likely to occur. The tendency of additions of cullet to minimize such separation is indicated.

Further tests have been made on five commercial container-glass compositions, which have raw materials of the same grain-size distribution as those in commercial use. These experiments indicate a varying effect of the addition of cullet in decreasing melting time. This variation cannot be explained by differences in the degree to which the various raw-material grain sizes are matched.

I. Introduction

For several years, the research laboratories of the Owens-Illinois Glass Company have been conducting a study of the melting rates of glass as a function of its composition and some of the results obtained have been published.[1] It was also considered desirable to study the influence of the grain sizes of the raw materials used on the melting rate of the glass batch.

Preliminary experiments in this phase of the study indicated that reproducible results were possible only when the grain sizes of all raw materials were identical, that is, all materials passing through a 40-mesh screen and remaining on a 60-mesh screen. Each attempt to vary the grain size of one raw material independently of those of the others used resulted in batch separation during melting, whether the quantity of glass being melted was 10 gm. or 2000 gm. The degree of separation was found to vary considerably from melt to melt, duplicate melts, in many instances, showing results that diverged by more than 100%.

These experiments indicated the necessity of providing some method of stirring during melting. Various mechanical stirrers were devised and tried in melts ranging in quantity from 10 to 200 gm. Several methods permitted duplication of results from test to test, but each presented difficulties in keeping parts aligned and in restricting working space. The stirring method described in section II was finally adopted because it was amply effective and because its simplicity commends its use for experimental studies.

II. Experimental Method and Apparatus

Sufficient batch materials to make exactly 10 gm. of glass of the desired composition were weighed out on an analytical balance and placed in a $^1/_2$-ounce ointment jar. The jar was closed and rotated end-over-end at 90 r.p.m. for 30 minutes. (Experiments on grab samples taken from batches so mixed have demonstrated that this method gives adequate and uniform mixing.)

Platinum crucibles were used which were 1 in. high, $1^1/_8$ in. in diameter at the base, $1^3/_8$ in. in diameter at the top, and 0.015 in. in wall thickness. (These crucibles must be cleaned in acid and reshaped in a steel die after each use. It is essential that crucibles remain exactly the same size and shape if consistent results are to be obtained.) The mixed batch was

---

* Presented at the Glass Division Autumn Meeting, The American Ceramic Society, Summit Hotel, Uniontown, Pa., September 15–16 (1943). Received March 4, 1944.

[1] (*a*) J. C. Potts, "Comparison of Rates of Melting Glasses Made from Sodium Carbonate, Dolomite Limestone, and Silica Sand," *Jour. Soc. Glass Tech.*, **23** [97] 129–40T (1939); *Ceram. Abs.*, **19** [4] 89 (1940).

(*b*) J. C. Potts, "Melting Rate of Soda-Lime-Silica Glasses as Influenced by Composition and Effect of Minor Constituents," *Jour. Amer. Ceram. Soc.*, **24** [2] 43–50 (1943).

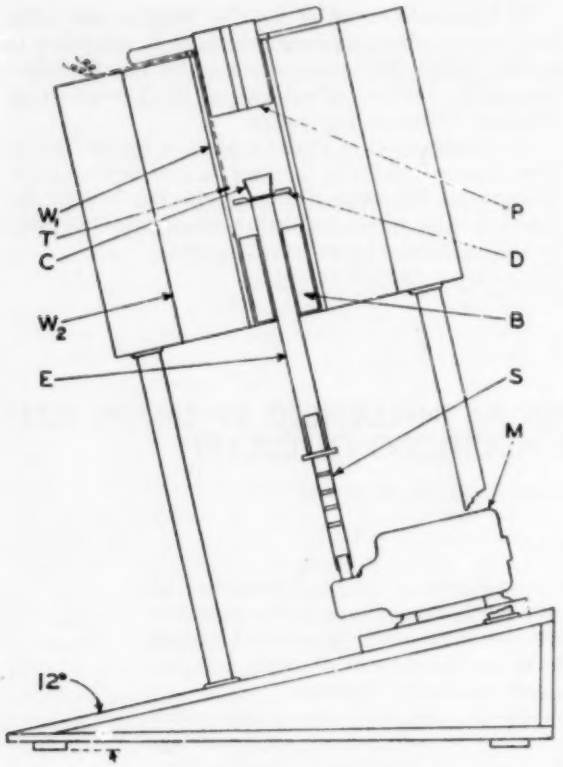


FIG. 1.—Diagram of furnace assembly.

poured through a stemless funnel into a crucible in such a manner as to distribute it evenly and with a minimum amount of batch separation.

The furnace, shown in Fig. 1, is a resistance, cascade-type furnace, with an outer winding (*W*-2) of Nichrome wire and an inner winding (*W*-1) of 80% platinum-20% rhodium alloy; approximately 64 ft. of No. 20 wire is used. The furnace tube is 3 in. in inside diameter and 12 in. long and has a working space $4^1/_2$ in. high. A thermocouple, *T*, attached to a temperature controller, maintains the temperature in the position occupied by the crucibles during the experiments at 2600° ± 3°F. A probing thermocouple is introduced once each day through the top plug, *P*, and the temperature is checked with a portable potentiometer.

The crucible, *C*, rests in a recessed Alundum disk *D*, which is attached to the Alundum extension tube, *E;* this tube in turn is supported and rotated by the motor drive shaft, *S* (see Fig. 1). Alundum tube *E* is kept in alignment without the use of an upper bearing by allowing the motor-drive shaft, *S*, to extend a short distance up the tube. The tube is held in place by a slot and pin coupling, which serves as a means of adjusting the height and also, when needed, as a clutch. The motor, *M*, is $^1/_{20}$ h.p., with built-in reducing gears so that shaft *S* rotates at 1 r.p.m.

The entire furnace assembly is tilted so that the crucible will rotate about an axis 12 degrees from the vertical. This rotation about an inclined axis produces a steady swirling action as the glass constantly flows toward the constantly shifting low point of the crucible. Two desirable effects result from this setup, (1) the unmolten batch, which is left on the crucible sides when the mass boils during the early stages of the melting, is washed down and (2) the entire batch is continuously stirred.

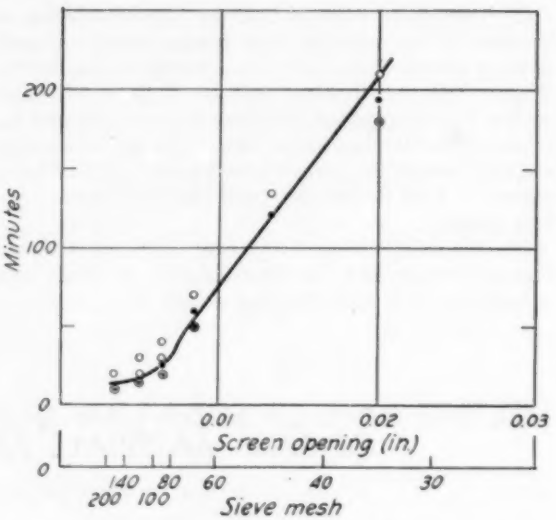


FIG. 2.—Effect of grain size on melting time (sand, soda ash, and limestone of same mesh size).

In running an experiment, the upper plug, *P*, of the furnace is removed, the crucible containing the weighed, mixed batch is inserted in place while the shaft is rotating, the plug is quickly replaced, and timing is started with a stopwatch. After the melt has been in the furnace for an arbitrary length of time, it is quickly removed, chilled, and examined under a low-power microscope (50 diameters). The melt is divided into two nearly equal areas by drawing a pencil circle about 4 mm. from the crucible sides. The area within the circle is referred to as the "center," and the annular area outside the circle is the "edge." The number of small and large particles of unmolten batch are counted and recorded separately in each area. The data for each melt, therefore, consist of a record of the composition, grain sizes of raw materials used, time and temperature of melting, and the number of particles in each of the four categories, that is, "large, center," "small, center," "large, edge," and "small, edge."

III. Experimental Results

(1) Limited Grain Sizes of Raw Materials

A glass of the following composition was selected for the initial phase of this study: SiO_2 73.8, R_2O_3 0.2, CaO 11.9, MgO 0.1, and Na_2O 14.0%. The commercial-quality raw materials used were Ottawa sand, St. Genevieve limestone, and Solvay soda ash. The various grain sizes of each raw material were carefully prepared by screening on U. S. standard sieves on a standard Ro-Tap sieving machine. The cullet used was of the composition shown above and had been

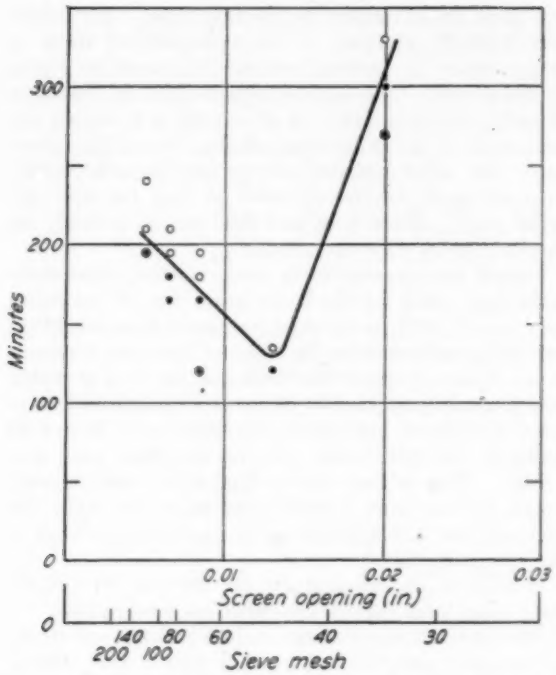


FIG. 3.—Effect of varying sand size; 40/60 soda ash and 40/60 limestone.

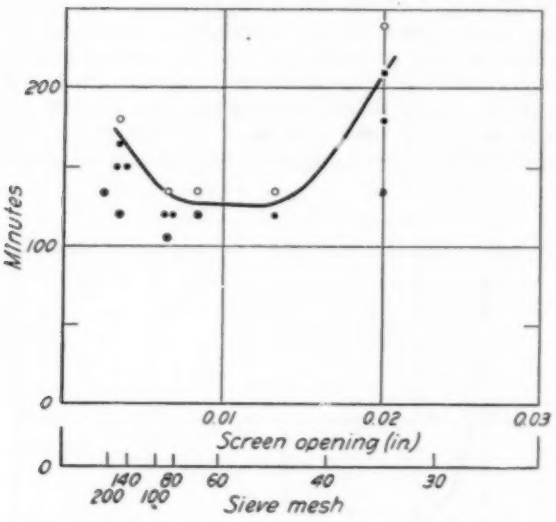


FIG. 4.—Effect of varying limestone size; 40/60 sand and 40/60 soda ash.

previously prepared by melting in platinum crucibles and by stirring, crushing, and remelting to obtain a homogeneous glass.

The actual experimental data are shown graphically in the figures; several experimental points are recorded opposite each point along the abscissa axis. The significance of these points is as follows: Open circles represent no particles of silica remaining undissolved; black dots represent 1- to 20- very fine particles of silica, usually found in the area referred to as the

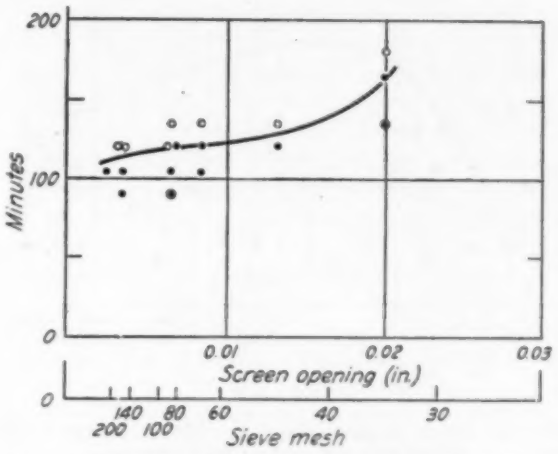


FIG. 5.—Effect of varying soda ash size; 40/60 sand and 40/60 limestone.

"edge"; and circles with center dots represent substantial quantities of undissolved silica grains.

The results shown in Fig. 2, in which sand, soda ash, and limestone are always matched in size, indicate a tremendous decrease in time required for the melt to become batch free as the grain size of the materials is decreased. This result seems to be logical and has probably been noted by everyone who has had experience in melting silicate glasses.

Figure 3 shows results obtained when the grain sizes of the soda ash and limestone have been maintained at 40-60 mesh and that of the sand has been varied. It is somewhat surprising to note that the minimum melting time occurs when 40-60 mesh sand is used. The increase in melting time as the grain size of the sand is decreased below 40-60 mesh is unusual and indicates to the authors that the demixing or separation of batch during melting is accelerated as the grain size of the sand continues to decrease in relation to the grain size of the soda ash and limestone.

The results in Fig. 4 show the effect of maintaining the grain size of sand and soda ash at 40-60 mesh and of varying the size of the limestone. The grain size of limestone seems to have less effect than that of sand (Fig. 3) because there is no measurable difference in melting time for limestone of 40-60, 60-80, or 80-100 mesh size. Extremely fine limestone (140-200 mesh) appears to accentuate demixing during melting.

Figure 5 shows the results of experiments in which grain sizes of sand and limestone remain constant and that of the soda ash is varied. It is evident that variations in the grain size of soda ash have less effect on demixing during melting than do variations of grain size of either sand or limestone. The use of 140–200 mesh soda ash accelerates (not decelerates) the melting time. The authors interpret this to be the effect of extremely fine soda ash that melts quickly, keeping the sand and limestone grains in relatively intimate contact with one another.

In studying the effects of glass composition on melting rate when using raw materials of fine grain size, the addition of cullet or of finely crushed glass did

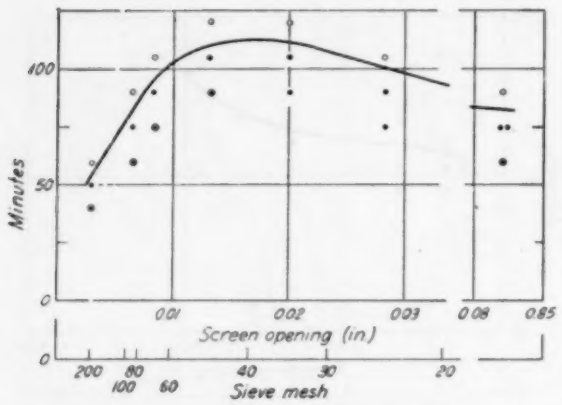


FIG. 6.—Effect of cullet size; *base glass:* 80/100 sand 40/60 soda ash, and 40/60 limestone.

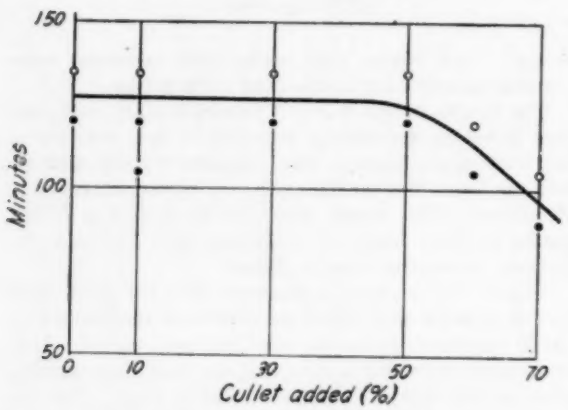


FIG. 7.—Effect of mount of 6/20 cullet added; *base glass:* 40/60 sand, 40/60 soda ash, and 40/60 limestone.

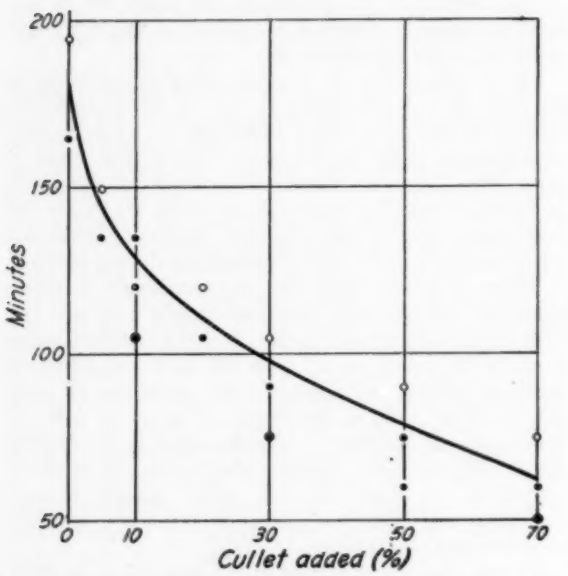


FIG. 8.—Effect of amount of 6/20 cullet added; *base glass:* 60/80 sand, 40/60 soda ash, and 40/60 limestone.

not seem to accelerate the melting time. The effect was decidedly contrary to the experience of those in this company in melting commercial glasses on a production scale. The authors believe that the function of cullet in the commercial glass melt is to retard the separation of batch materials during the melting process. The cullet probably softens and becomes sticky at a relatively low temperature so that the raw material grains adhere to it and thus remain in fairly intimate contact with one another.

Before the present tests were started, laboratory tests were made in which the grain size of the cullet was varied; 50% of the glass was made from the batch and the other half from the cullet of the same composition. Figure 6 shows the results of the test in which 80-100 mesh sand and 40-60 mesh soda ash and limestone were used; the cullet grain size varied from 6-20 down to 100-200 mesh. The results were most surprising. The authors see no good reason why a maximum melting time should occur when the grain size of the cullet was approximately equivalent to that of the raw materials.

A possible explanation for the decrease in melting time when large particles of cullet are used follows.

The cullet should begin to soften and become sticky at temperatures below those at which the melting reactions between the raw materials assume appreciable proportions. Sand, limestone, and soda ash particles should adhere to these sticky surfaces, thus reducing the amount of segregation during melting. The weakness of this theory is the fact that as the size of the cullet particles decreases the ratio of surface area to weight increases so that more raw-material grains should stick to a given weight of small particles than to the same weight of large particles. The definite experimental observation, however, is that an increase of the

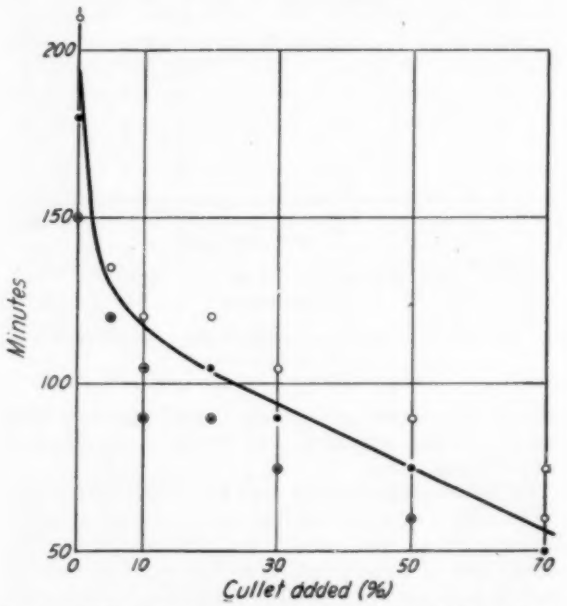


FIG. 9.—Effect of amount of 6/20 cullet added; *base glass:* 80/100 sand, 40/60 soda ash, and 40/60 limestone.

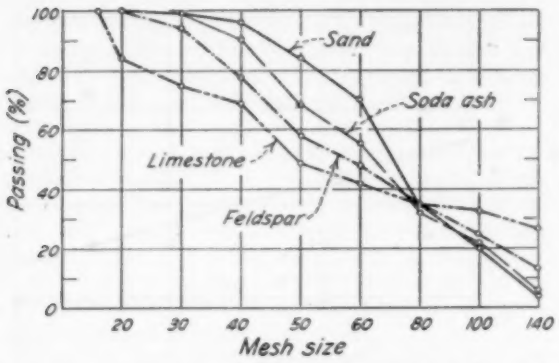


FIG. 10.—Glasses No. 1 and No. 2, raw-material grain sizes (mesh size, U. S standard screens).

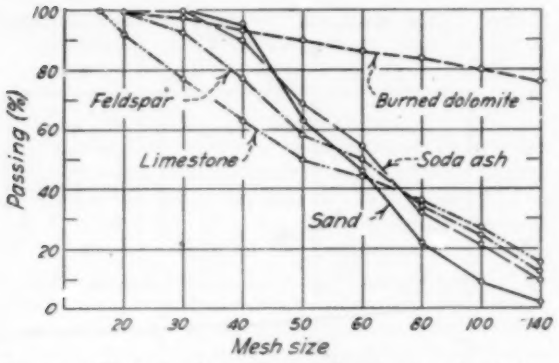


FIG. 11.—Glass No. 3, raw-material grain sizes (mesh size U. S. standard screens).

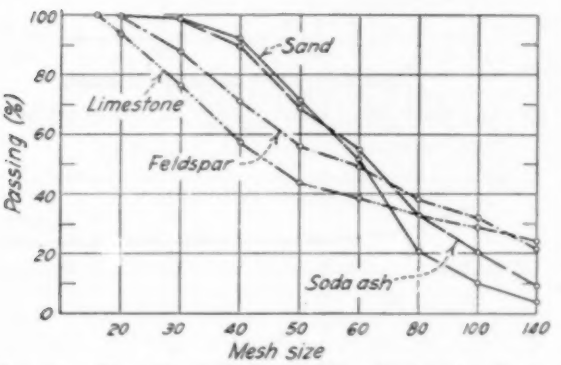


FIG. 12.—Glass No. 4, raw-material grain sizes (mesh size U. S. standard screens).

cullet size beyond that of the raw-material grains increases its effectiveness.

For sizes below 60-mesh, the mechanism seems similar except that cullet is the outside phase and adheres to the surfaces of the raw-material grains. Prediction, in this case, agrees well with experiment, that is, a decrease in cullet size (thereby increasing its covering power) decreases the time required to obtain batch-free glass.

Inasmuch as 6-20 mesh cullet is quite easily prepared and seemed to be more effective in decreasing separation

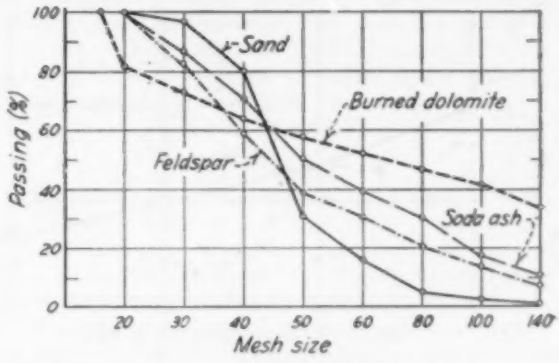


FIG. 13.—Glass No. 5, raw-material grain sizes (mesh size, U. S. standard screens).

during melting than did the 40-60 or 60-80 mesh cullet, the 6-20 mesh cullet was used in all subsequent experiments.

Figure 7, in which all of the raw materials were 40-60 mesh (the cullet, 6-20 mesh), shows that up to a point where 50% of the finished glass is made from cullet no benefits are derived in a reduction of melting time. The results confirm earlier work in which extremely fine grain sizes of raw materials were used. When the cullet is decreased beyond 50%, for example, to 70%, the melting time decreases. The authors have no explanation of this result unless it be one of dilution.

Figure 8 shows the effect of the addition of 6-20 cullet on the melting time of glass made from 60-80 mesh sand and 40-60 mesh soda ash and limestone. A continuous decrease of melting time occurs as the percentage of glass made from the cullet is increased. The slope of the curve indicates that additions of the first small amounts of cullet, that is, when 5 to 10% of the glass is made from cullet, are most effective in reducing the melting time.

In Fig. 9, in which 80-100 mesh sand and 40-60 mesh soda ash and limestone were used, the effect of adding the first small amounts of cullet on the reduction of melting time is even more pronounced.

The results in Figs. 8 and 9 definitely indicate that cullet minimizes batch separation during melting. A comparison of Figs. 8 and 7 shows that it is necessary to add cullet only in sufficient amount to make 10% of the finished glass from cullet in order to realize the expected effects of decreasing grain size of sand on the melting rate of glass. A comparison of Figs. 9 and 7 shows that beyond the point of cullet addition, where about 5% of the glass is made from cullet, the beneficial effects of fine-grain sand on rapid melting are realized.

(2) Raw Materials of Commercial Grain-Size Distribution

In the foregoing studies, the grain sizes of all of the raw materials were carefully controlled. Further studies were made on the effect of the addition of cullet on the melting rate of glass batches in which the grain-size distribution of the raw materials was typical of those encountered in commercial practice.

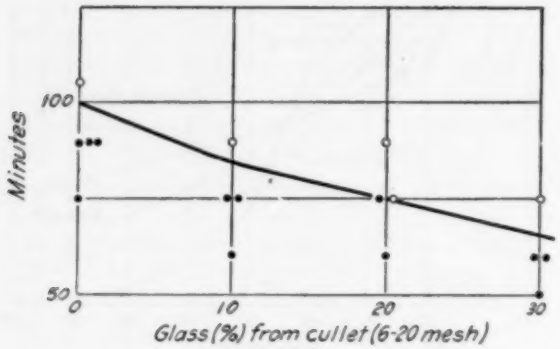


FIG. 14.—Glass No. 1, effect of cullet on time to get batch free at 2600°F.

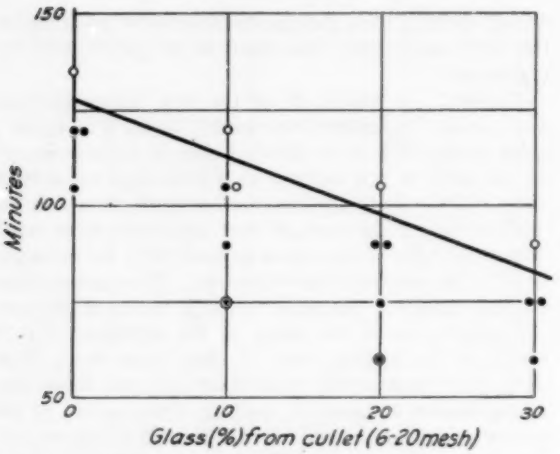


FIG. 15.—Glass No. 2, effect of cullet on time to get batch free at 2600°F.

TABLE I

BATCH COMPOSITION AND THEORETICAL GLASS COMPOSITION OF COMMERCIAL SAMPLES

Composition No.	1	2	3	4	5
Batch composition					
Sand	2000	2000	2000	2000	2000
Soda ash	765	690	635	665	650
Burned dolomite			200		395
Limestone	670	610	335	665	
Feldspar	515	260	170	290	130
Barytes			30	30	30
Theoretical glass composition (%)					
SiO_2	70.0	72.2	71.7	71.3	71.15
R_2O_3	3.2	1.9	1.25	1.95	1.2
CaO	11.0	11.2	10.2	11.4	8.1
MgO	0.2	0.1	2.8	0.8	5.5
BaO			0.65	0.65	0.65
$Na_2O + K_2O$	15.6	14.6	13.4	13.9	13.4
Time batch free at 2600°F.	7.5	9.0	8.5	7.0	8.5

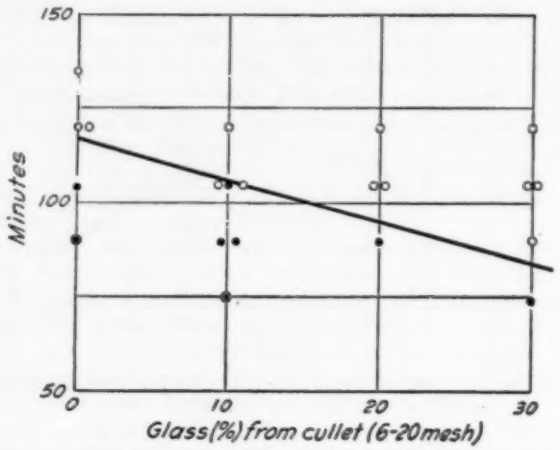


FIG. 16.—Glass No. 3, effect of cullet on time to get batch free at 2600°F.

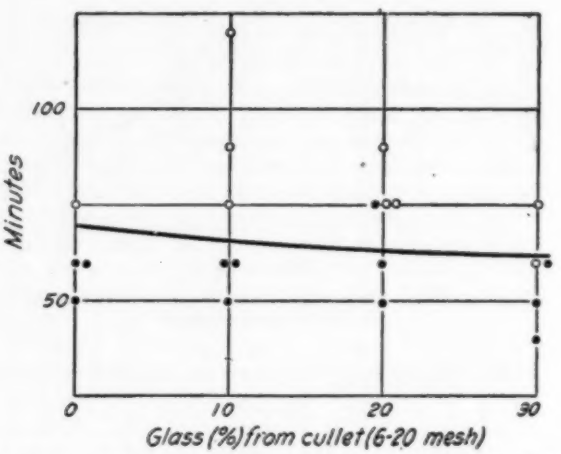


FIG. 17.—Glass No. 4, effect of cullet on time to get batch free at 2600°F.

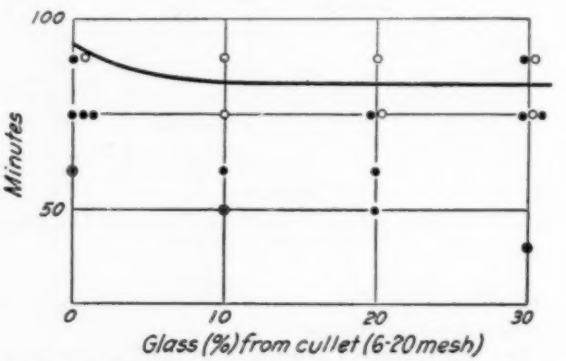


FIG. 18.—Glass No. 5, effect of cullet on time to get batch free at 2600°F.

Five commercial bottle-glass batches were selected, and the raw materials from actual commercial production of these glasses were used for the experiment. Table I shows the batch compositions and theoretical glass compositions of each of these glasses. The melting time required to obtain batch-free glass is also given. These results were obtained with 100-140 mesh sand and 100-200 mesh size for the other raw ma-

terials. The method used has been described previously.[1] An examination of the time required for the five compositions to become batch free in this test shows little significant effect of composition on melting. Figures 10 through 13 show the grain-size distribution of the various raw materials used in the laboratory experiments as well as those used in commercial practice of compositions 1, 2, 3, 4, and 5, respectively. These figures show that the single raw material in which the grain size is poorly matched with the other raw materials is the burned dolomite for glass No. 3 (Fig. 11). In all of the other compositions, the materials are matched in grain-size distribution about as well as is usually found in commercial practice.

Figures 14 through 18 show the effect of adding 6-20 mesh cullet to the batches used in making the five glasses; these figures indicate that, with no cullet, the relative ease of melting the five glasses may be ranked in the following order: Nos. 4, 5, 1, 3, and 2. As the amount of cullet incorporated with the batch is increased, no significant effect is indicated for glasses Nos. 4 and 5, whereas Nos. 1, 2, and 3 require substantially less time to become batch free.

Strange as it may seem, it is the commercial practice in the factories melting these five glass compositions to use all of the cullet they can obtain for compositions Nos. 1, 2, and 3 and to use only moderate amounts (10 to 15% by weight of the finished glass) in compositions Nos. 4 and 5. This practice appears to indicate a good relation between laboratory experiments on a batch-free basis and plant practice, which is on a seed-free basis. The authors offer no explanation for the apparent beneficial effects of cullet addition in reducing the time necessary for compositions Nos. 1, 2, and 3 to become batch free in contrast to the apparent ineffectiveness of the additions of cullet to compositions Nos. 4 and 5.

IV. Summary

The following conclusions seem to be justified from the data presented:

(1) When grain sizes of all raw materials are the same, glasses become batch free at a rapidly increasing rate as the mean grain sizes are reduced.

(2) If the grain sizes of the materials are different, the time required for the glass to become batch free is increased, probably due to batch separation during melting.

(3) When the grain sizes of the raw materials differ, the addition of cullet tends to minimize separation during melting and thus reduce the time required for the glass to become batch free. The first increments of cullet added appear to have the most marked effect in reducing the time required to obtain batch-free glass.

(4) In the case of raw materials that have grain-size distributions typical of those found in commercial use, the effectiveness of cullet additions seems to vary. This variation of results, however, cannot be explained solely on the basis of matching or mismatching grain-size distribution.

General Research Laboratories
Owens-Illinois Glass Company
Toledo 1, Ohio

SUGGESTIONS FOR SOLUTION OF DIFFICULT GLAZE-FIT PROBLEMS*

By C. G. Harman

Abstract

The methods and principles are discussed by means of which suitable glazes for special purposes may be prepared. Examples are given of glazes for low-expansion bodies and also of durable low-temperature glazes.

I. Introduction

(1) Glaze-Fit Problem

As an example of problems in glaze fit, low-expansion cordierite bodies have not been glazed by the usual conventional glazes because it has been impossible to find sufficiently low-expansion glazes that mature at the permissible temperatures. Similar problems may be encountered in special low-temperature glazes for standard bodies. The increase in the variety and application of specialized bodies will certainly increase the demand for corresponding specialized glazes to overcome the fairly definite limitations of the conventional glaze types.

The scope and possibilities of the development of special glazes will therefore be examined, particularly from the viewpoint of glaze fit because it is one of the critical limitations to be met.

(2) Relation of Stresses in Glaze to Glaze Fit

Glaze fit depends on the magnitude and character of the stresses developed in the glaze. Because glazes are weak in tension, very small tensile-stress values result in crazing. The compressive strength of the glaze, however, is very high, and a glaze can sustain quite high compressive stresses without showing any ill effects. It is common practice in fact to maintain, intentionally, a high compressive stress in the glaze.

(3) Effect of Variables on Degree of Stress

A number of factors may be involved in the development of stress in a glaze layer; chief among these factors is the ratio of volume changes in the body to volume changes in the glaze. If a body and its attached glaze layer have a common area of contact at high temperatures, then any tendency during cooling of either to depart from the size of their common area results in stress formation, and if carried far enough, rupture oc-

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (White Wares Division). Received April 5, 1944.

curs in one or the other member. Other factors, such as strain temperature of the glaze, rate of cooling, especially through the annealing range of the glaze, and glaze thickness and its strength and elasticity have modifying influences on glaze fit. Diffusion, vaporization, and glaze adherence may also be important.

The purpose of this paper was to consider the different ways in which these factors may be made to operate to secure suitable glaze fit.

II. Processing and Stress Development in Glazes

(1) Glaze Maturing Point Above Liquidus Temperature and Reversible Thermal Expansion of Glazes Lower Than That of Body

(*A*) *Glaze Entirely Glassy:* This is the conventional type of glaze with essentially no crystalline matter. The physical characteristics of this type bear a direct relation to their chemical compositions. The softer or lower maturing glazes usually have the highest thermal expansions, and the glazes having the lowest thermal expansions can be obtained only at the highest temperatures. Some other types of glazes are less restricted by these limitations.

(*B*) *Undissolved Crystalline Matter in Glazes:* This glaze is closely related to type 1–A. Its principal distinction is that it contains undissolved crystalline matter, which contributes to its thermal expansion. This distinction is important because the thermal expansions of crystal phases do not bear the same relation to chemical composition as do glasses. The thermal expansion of a glaze may therefore be lowered or raised by the inclusion of undissolved crystalline matter.

The use of certain opacifiers and color stains or simply undissolved batch usually falls under this classification. It is quite feasible, however, to introduce low-expansion crystalline matter, which does not dissolve in the glaze, to obtain better glaze fit. The materials suitable for this purpose would depend on the firing temperature and the thermal expansion of the glaze and also on the relative insolubility of the material in the molten glaze. The effect of inversions, if any, of the crystal phase on the stress development would, of course, depend on (*a*) direction of volume change, (*b*) magnitude of volume change, and (*c*) temperature of inversion.

The application of this method is obviously limited by the proportion of crystalline matter that the glass can carry and by available materials. With the more fluid glasses, as much as 30% by volume of fine crystalline material may be incorporated. Too few physical constants are available to permit listing suitable crystalline additions.

(*C*) *Glazes Containing Crystalline Matter Derived from Devitrification on Cooling:* This glaze is basically the same as 1–B except that the crystalline phases are not added as batch constituents but are derived from partial crystallization of the cooling glaze. The only requirement of the crystalline matter in this case is that it contributes to lowering the thermal expansion of the glaze. A good example of this type would be one that precipitates $2ZnO \cdot SiO_2$ on cooling. These glazes usually are low in silica.

Glazes of types 1–B and 1–C can be made to fit lower expansion bodies than is possible with type 1–A, but the extension of the limit is not great and other types must be considered to extend the range drastically.

(2) Maturing Point of Glaze Above Liquidus Temperature and Reversible Thermal Expansion of Glaze Higher Than That of Body

(*A*) *Glazes Containing Crystalline Matter Derived from Devitrification During Cooling of Glaze:* The density of a crystalline phase is generally greater than that of the corresponding liquid or glassy phase. When a glass or a glaze partially devitrifies or partially crystallizes, the crystals which separate usually have a higher density than that of the glass. The glaze as a whole in such cases undergoes a decrease in volume as a result of crystallization. This decrease, however, is not always the case, and it is possible to compound glazes in which the crystals have a greater specific volume than the residual glass, thus causing the glaze to increase in volume during the separation of the crystals. This swelling acts to oppose the action of thermal expansion (thermal contraction on cooling). The net effect of cooling such a glaze is a small change in size from the high temperature to room temperature. Even though the glaze has a reversible thermal expansion above that of the body, the swelling caused by crystallization may act so as to produce the effects of lower thermal expansion during the initial cooling and put the glaze in compression.

A typical example of the stress variation during the cooling of a glaze of this kind is shown in Fig. 1. In this example, the viscosity of the glaze becomes high enough at the temperature marked "strain point" to permit the development of a small initial tensile stress. On continued cooling, beginning at the point marked "crystallization starts," the small tensile stresses are quickly wiped out. The compressive stresses increase as the temperature drops until they reach a maximum value at the point marked "thermal expansion exceeds swelling caused by crystallization." Cooling from this point on results in a continual decrease in compression but retains appreciable compression at room temperature in a well-balanced glaze.

To obtain a glaze that will show sufficient expansion during crystallization, it is necessary to form a fusion of quite high density. A high lead glaze that would precipitate an alkaline earth silicate on cooling would serve as an illustration. The residual lead-containing glass in this case may have a density of 5 compared to 3.5 for the alkaline earth silicate.

A glaze of the following composition will fit a whiteware body if it is allowed to crystallize, but it will craze if no crystals are allowed to form:

$$\left.\begin{matrix} 0.12\ K_2O \\ 0.48\ PbO \\ 0.25\ BaO \\ 0.15\ ZnO \end{matrix}\right\}\ 0.18\ Al_2O_3\ \ 1.80\ SiO_2$$

The crystalline phase in this glaze has been identified as hyalophane (orthoclase containing celsian in solid

solution) and has a considerably higher specific volume than the residual lead-containing glass.

A glaze of the following composition will fit a cordierite body as well as higher expansion bodies, although it has a reversible coefficient of expansion of 73×10^{-7} per °C.:

$$\left.\begin{matrix} 0.4613\ PbO \\ 0.1636\ MnO \\ 0.2683\ CuO \\ 0.1067\ CoO \end{matrix}\right\} 0.055\ Al_2O_3 \quad 0.4904\ SiO_2$$

This glaze presumably operates according to the principles under discussion although the crystalline phases have not been identified.

Glazes of this type are limited to those of high density and presumably of low softening points. There must be as much difference as possible between the density of the crystal phase and the glass, the glass having the higher density.

(3) Maturing Point of Glaze Lower Than Its Liquidus Temperature and Reversible Thermal Expansion Lower Than That of Body

(*A*) *Glaze Entirely Glassy:* Glazes lower in expantion than those of type 1–A must be fused at temperasures too high for many glazing operations. Such compositions may be prepared as a glass at a high temperature in a separate operation, finely ground, applied to the ware, and sintered onto the ware at a relatively low temperature.

Only glasses of certain general characteristics are suitable for this process. They must be capable of being sintered to a continuous, vitreous layer without devitrification. In other words, there should be a fairly wide temperature interval between the softening point of the glass and the temperature of rapid devitrification. Some glasses very high in silica, with a moderate amount of boric acid, and low in metallic oxides are suitable.

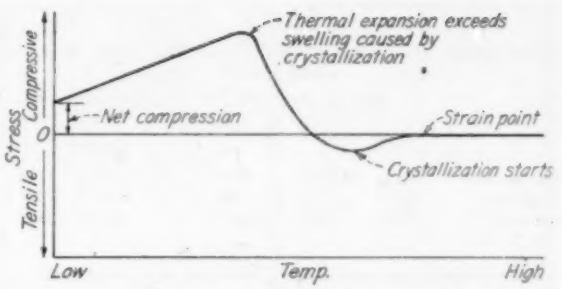


FIG. 1.—Typical example of stress variation in glaze 1–B during initial cooling.

The thoroughly melted glass should be ground to a fineness of 10 microns or less, suspended in water, and applied by dipping or spraying. The maturing temperature of such glazes is quite low; for example, a glaze high in SiO_2 with a coefficient of expansion of 20×10^{-7} per °C. was matured at 870°C. (1600°F.).

The low-maturing temperatures and virtual lack of flow at maturity of this type of glaze seem to hold promise as a low-temperature coating for underglaze decorations.

(*B*) *Glaze Contains Undissolved Crystalline Matter:* Type 3–A may be modified slightly by the addition of some low-expansion material such as cordierite or beryl.

DEPARTMENT OF CERAMIC ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

STRONTIA AND ITS PROPERTIES IN GLAZES*

BY EARL S. MCCUTCHEN

ABSTRACT

Strontia has proved to be a strong flux and a desirable glaze ingredient when it is used to replace PbO, ZnO, and CaO in a typical dinnerware glaze. By including it in the frit, the fluidity of the glaze was increased to a marked degree when it was substituted for ZnO and CaO and it also lowered the deformation temperature in the replacement of the latter oxide. Thermal-expansion tests indicate that strontia has practically the same effect as lime on glaze expansion. Glazes of excellent visual and physical properties were obtained in a series of low-lead and leadless compositions containing strontia.

I. Introduction

(1) General

Strontium is an alkaline earth metal related to calcium and barium in its chemical properties, but it possesses more individual characteristics in ceramic melts. It is found chiefly as the sulfate, celestite, in large deposits in this hemisphere as well as in other parts of the world. It is not a common element in the sense of having a wide range of uses. Its primary importance until now has resulted from the crimson color it imparts to the flame for use in flares, tracer bullets, and other pyrotechnics. Only recently, however, has it been produced in sufficiently ample volume to warrant investigation as to its possible value in the ceramic industry.

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, April 5, 1944 (Design Division). Received April 11, 1944.

(1944)

TABLE I

PROPERTIES OF STRONTIUM, CALCIUM, AND BARIUM COMPOUNDS

	Melting point (°C.)			Carbonate (solubility in water)	
	Metal	Oxide	Metasilicate	(gm.)	(°C.)
Strontium	752	2430	1580	0.0011	18
Calcium	810	2572	1540	.0014	25
Barium	850	1923	1604	.0022	18

TABLE II

EUTECTIC MELTING TEMPERATURES

Weight proportion	Melting temp. (°C.)
SrO 46.5, SiO_2 53.5	1358
CaO 37, SiO_2 63	1436
BaO 47, SiO_2 53	1374

(2) Properties

Table I lists the values for significant properties of some strontium, calcium, and barium compounds.

A preliminary examination of the $SrO–Al_2O_3–SiO_2$ system by Watts[1] indicates that its eutectic deforms at a lower temperature than either the $CaO–Al_2O_3–SiO_2$ or $BaO–Al_2O_3–SiO_2$ eutectics. Additions of SrO to a base glaze have been reported in one instance to decrease the fusibility[2]; in another, replacement of BaO by SrO increased the fusibility of a glaze.[3] Kreidl[4] states that strontium does not form a peroxide as does barium; as a result, much of the difficulty encountered in fining barium glasses, which is caused by the release of oxygen in the melt, can be eliminated by the partial replacement of BaO by SrO.

II. Experiments

A typical cone 4 dinnerware glaze was used as a base glaze and SrO was introduced as a molecular replacement of PbO, ZnO, and CaO, respectively.

Molecular formula of base glaze

$$\left.\begin{matrix}0.06\ Na_2O\\0.12\ K_2O\\0.43\ CaO\\0.13\ ZnO\\0.26\ PbO\end{matrix}\right\}\ 0.27\ Al_2O_3\ \left\{\begin{matrix}2.60\ SiO_2\\0.31\ B_2O_3\end{matrix}\right.$$

Fritted portion

$$\left.\begin{matrix}0.045\ Na_2O\\0.09\ K_2O\\0.23\ CaO\end{matrix}\right\}\ 0.036\ Al_2O_3\ \left\{\begin{matrix}0.73\ SiO_2\\0.31\ B_2O_3\end{matrix}\right.$$

PbO added as eutectic frit

$$PbO \qquad 0.254\ Al_2O_3 \qquad 1.91\ SiO_2$$

The strontia substitutions were added as follows to the glaze in the same manner as the replaced oxide: (1) in the frit to replace the PbO, (2), in the mill addition to replace the ZnO, and (3) one half in each to replace the CaO. The molecular portion of each glaze which was fritted thus remained the same.

One-hundred pound batches of these glazes were milled in the laboratory mills of a dinnerware plant. Four dozen 7-inch semivitreous plates were dipped in each glaze at two different plants and fired in their respective tunnel kilns. Rings and bars, cast for glaze stress and modulus of rupture tests, were dipped and glost fired along with the plate specimens.

To compare the molecular and weight introductions of SrO, a soda-lime glass composed of Na_2O 12, CaO 11, Al_2O_3 8, and SiO_2 69% was used, the Al_2O_3 being added to prevent devitrification. Molecular and weight replacements of the lime were made with strontia, and the resulting glasses were studied relative to their softening temperatures, fused viscosity, and thermal expansion.

A technical grade of strontium carbonate analyzing 95% $SrCO_3$ was used throughout this investigation as the source of SrO. The impurities consisted of SiO_2 2.5, CaO 1.6, and a small percentage of $SrSO_4$, none of which was found to be objectionable.

III. Tests and Results

(1) Glazes

(*A*) *Visual Properties:* The glazes with SrO replacements of ZnO and CaO were equal if not superior to the base glaze. In replacing the PbO, the texture of the glaze showed a tendency toward egg-shelling because of increased viscosity; samples of this glaze, however, which received higher than average heat-treatment were excellent leadless glazes. None of the glazes crazed or blistered.

(*B*) *Deformation Temperature:* Cone-deformation tests were made of each glaze in three batch forms, namely, (1) raw, (2) partially fritted as used in the plant trials, and (3) entirely fritted. Cones were made from each batch after thorougly mixing and screening the glaze powders through a 100-mesh seive. The firing was done in a Westinghouse electric furnace in six to seven hours. Values for the deformation temperatures are listed in Table III.

TABLE III

CONE DEFORMATION TEMPERATURES OF GLAZES

	Temp. (°C.)		
	Raw glaze	Partially fritted	Entirely fritted
Base glaze	878	888	796
Replacement			
PbO	940	970	882
ZnO	906	897	804
CaO	896	882	780

(*C*) *Fused Viscosity:* Comparisons of the fused viscosities of the glazes were made with the true cone as employed by Beam.[5] Cones measuring $1^1/_2$ in. in diameter at the base and $1^3/_4$ in. high were formed from the same batches as were used for the deformation studies

[1] A. S. Watts, Ohio State Univ., unpublished work.
[2] E. C. Hill, "Some Data on Development of Terra Cotta Glazes," *Jour. Amer. Ceram. Soc.*, **3** [1] 13–25 (1920).
[3] C. E. Ramsden, "Study of Chromium Red Glaze," *Trans. Ceram. Soc.* [England], **12**, 239–60 (1912–1913).
[4] N. J. Kreidl, "Possibilities of Strontia in Ceramics," *Foote Prints*, **14**, 19 (1941).
[5] J. R. Beam, "Effect of Opacifiers on Fused Viscosity of Feldspathic Glazes," *Jour. Amer. Ceram. Soc.*, **26** [7] 205–12 (1943).

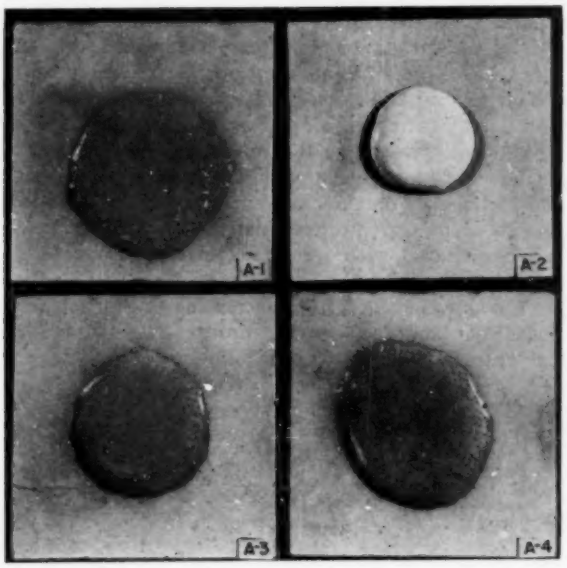


FIG. 1.—Fused viscosities at cone 4 of raw batches of base glaze (A–1) and SrO replacements of PbO (glaze A–2), ZnO (glaze A–3), and CaO (glaze A–4).

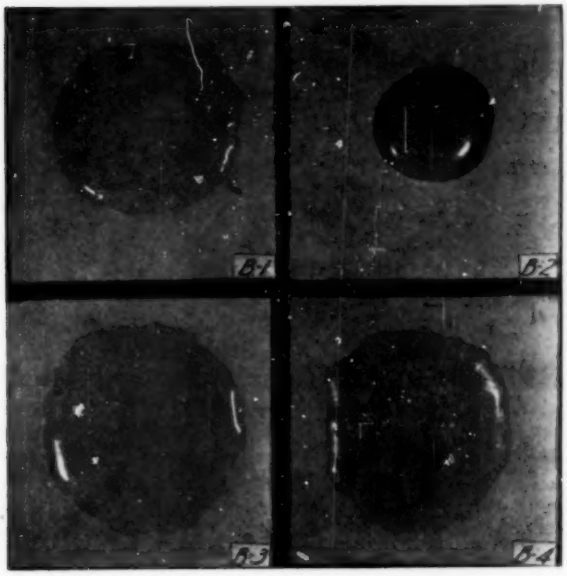


FIG. 2.—Fused viscosities at cone 4 of partially fritted glazes; base glaze (B–1) and SrO replacements of PbO (glaze B–2), ZnO (glaze B–3), and CaO (glaze B–4).

by packing the dry powder in a brass mold. Each cone was fired on an individual bisque tile, and the three batches were fired as a group to cone 01 and cone 4, each in 24 hours. The area of each fused cone (Figs. 1, 2, 3), measured with a planimeter, was then taken as the viscosity factor for the respective glaze.

A study of these factors (Table IV) revealed that no improvement of the fluidity occurred in the raw batches by the SrO substitutions. In the fritted batches, how-

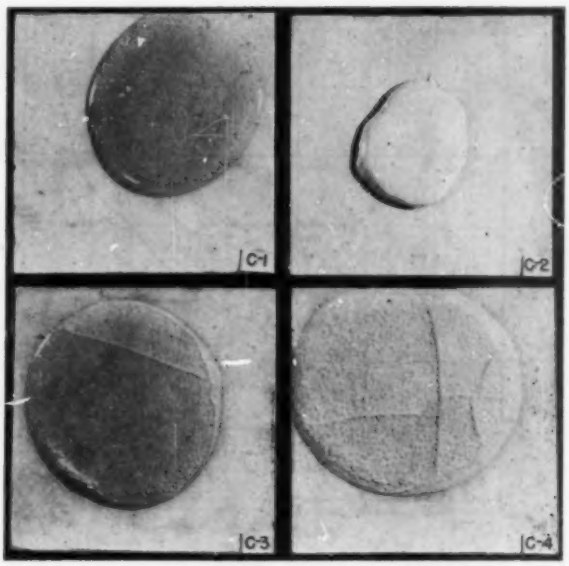


FIG. 3.—Fused viscosities at cone 4 of fritted batches of base glaze (C–1) and SrO replacements of PbO (glaze C–2), ZnO (glaze C–3), and CaO (glaze C–4).

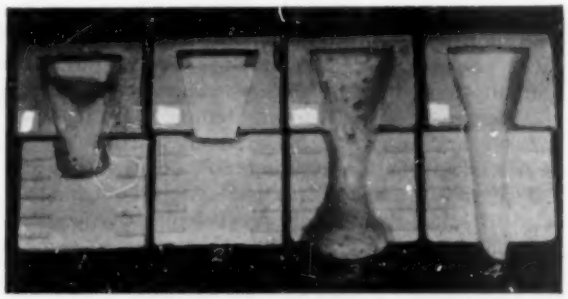


FIG. 4.—Inclined plane viscosities at cone 09 of base glaze (1) and SrO replacements of PbO (glaze 2), ZnO (glaze 3), and CaO (glaze 4); glazes partially fritted as used in plant trials.

TABLE IV

FUSED VISCOSITIES OF GLAZES

	Viscosity factor at cone 01		
	Raw glaze	Partially fritted	All fritted
Base glaze	3.89	4.25	3.70
Replacement			
PbO	2.05	2.50	2.20
ZnO	3.03	4.55	4.34
CaO	3.84	3.80	5.54
	Viscosity factor at cone 4		
Base glaze	5.42	6.42	6.68
Replacement			
PbO	2.25	2.56	2.80
ZnO	3.94	8.36	8.31
CaO	4.93	7.63	9.97

ever, a much greater fluidity resulted when the ZnO and CaO were replaced. Fusion block tests at cone 09 (Fig. 4) made with the partially fritted glazes used in

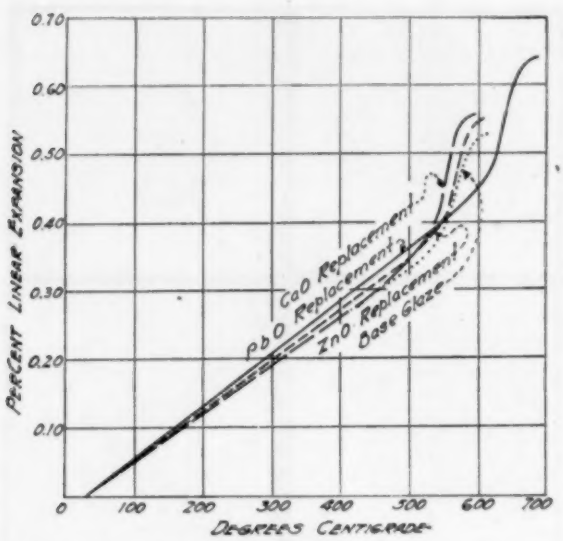


FIG. 5.—Thermal-expansion curves of base glaze and strontia replacements of PbO, ZnO, and CaO.

the plant tests also showed a definite lowering of viscosity by the SrO replacements of ZnO and CaO.

(*D*) *Solubility:* Determinations of water and acid solubility were made with samples taken from the glaze frits prepared for the deformation and viscosity tests. A 2.0000-gm. sample of 150- to 200-mesh frit was boiled for 5 hours in a flask containing 150 cc. of distilled water and fritted with a reflux condenser. After reweighing the dried frit, the loss in weight was calculated as percentage solubility. This procedure was repeated using a 10.0000-gm. sample of 20- to 28-mesh frit and 150 cc. of 4% acetic acid. A third test was run with 10.0000 gm. of 20- to 28-mesh frit and 150 cc. of 20% hydrochloric acid.

The water solubilities showed an increase in the case of the PbO replacement compared with the base glaze but a decrease in the ZnO and CaO replacements. The acid solubilities were the reverse of this, greater in the ZnO and CaO replacements and less in the PbO replacement.

	Weight loss (%)		
	Water	4% acetic acid	20% HCl
Base glaze	0.28	0.18	10.71
Replacement			
PbO	.56	.11	3.45
ZnO	.24	.23	11.90
CaO	.21	.21	13.76

(*E*) *Thermal Expansion:* Conical specimens of each glaze, ground from annealed samples, were used in the interferometer for thermal-expansion determinations. The expansion-versus-temperature curves (Fig. 5) indicated that strontia substituted for PbO increased both the expansion and transformation temperatures. Replacement of the ZnO caused a slight increase in expansion. When the lime was replaced, no change in expansion occurred up to 450°C., but as in the case of the ZnO, the transformation temperature was lowered.

(*F*) *Ring Test:* Evaluation of the stresses between the glazes and bodies was made with the ring test as developed by Schurecht and Pole[6] and modified by Bell.[7] Rings cast from the two plant bodies ($2^3/_4$ in. in diameter, $^1/_2$ in. high, $^1/_4$ in. thick, fired dimensions) and glazed only on the outer surface were cut between previously measured reference marks, and the distance was remeasured with a micrometer microscope. All glazes were found to be in compression on both bodies, the amount of compression decreasing as SrO replaced ZnO, PbO, and CaO, in that order. The averages of six values for each glaze are as follows:

	Compression (mm.)	
	Body 1	Body 2
Base glaze	0.104	0.145
Replacement		
PbO	.088	.117
ZnO	.092	.128
CaO	.057	.113

(*G*) *Flexural Strength:* Flexural strength tests were made on cast bars (7 in. long, 1 in. square), glazed and unglazed, to determine the effect of each glaze on the strength of the bodies. The values, calculated as modulus of rupture, were the averages of ten specimens each.

	Modulus of rupture (lb./sq. in.)	
	Body 1	Body 2
Unglazed	5256	4591
Base glaze	5363	4881
Replacement		
PbO	4945	5175
ZnO	5046	4817
CaO	5474	5131

On body 1, only the base glaze and the lime-replacement glazes improved the strength, whereas all four glazes increased the strength of body 2.

(*H*) *Autoclave and Thermal Shock:* Twelve plate specimens of each glaze were subjected to 150 lb. of steam pressure in the autoclave for one hour. After five cycles, the following numbers had passed without failure:

	Glaze No.
Base glaze	11
Replacement	
PbO	9
ZnO	7
CaO	11

Thermal quenching tests were made by heating twelve plate specimens at 200°C. for one hour in an electric oven and plunging them into water at 25°C. After the completion of twenty cycles of this treatment,

[6] H. G. Schurecht and G. R. Pole, "Methods of Measuring Strains Between Glazes and Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **13** [6] 369–75 (1930).

[7] W. C. Bell, "Evaluation of Glaze-Fit Test Methods," *ibid.*, **23** [6] 163–66 (1940).

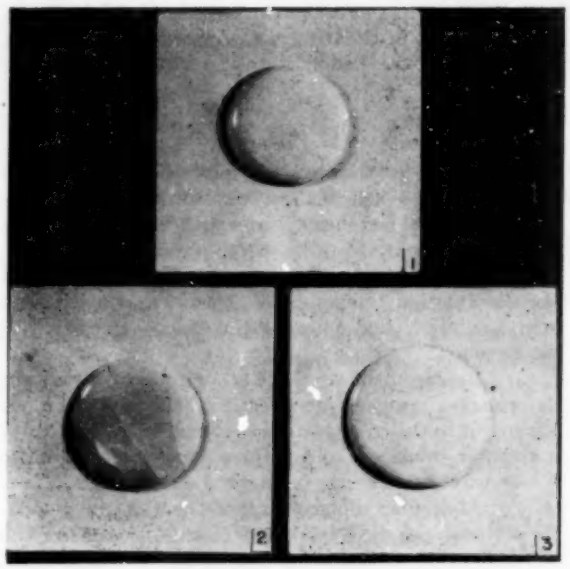


FIG. 6.—Fused viscosities of soda-lime glass (1), weight replacement (2), and molecular replacement (3) of CaO by SrO.

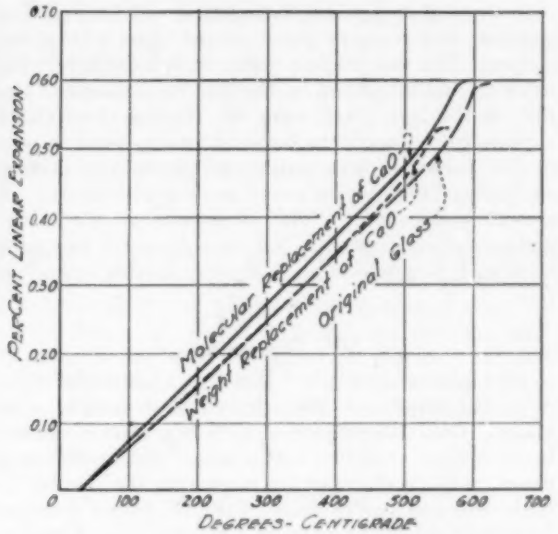


FIG. 7.—Thermal-expansion curves of soda-lime glass and weight and molecular replacements of CaO by SrO.

only one each of the ZnO and CaO replacements and none of the base- and PbO-replacement glazes had crazed.

(2) Glasses

Molecular versus weight replacement of the lime in the soda-lime glass was studied by determining the thermal expansions, deformation temperatures and fused viscosities (Fig. 6) in the manner described for the glazes. Values for the last two properties revealed that both were lowered by each replacement.

	Deformation temp. (°C.)	Viscosity factor (cone 3)
Soda-lime glass	794	2.94
Weight replacement	753	3.50
Molecular replacement	759	4.00

Thermal-expansion curves of the three glasses (Fig. 7) showed that no change in expansion occurred up to 400°C. when strontia replaced the lime on a weight basis, but the molecular replacement caused a rise in expansion.

IV. Experimental Glazes

A series of experimental glazes was developed in the laboratory employing strontia in a variety of glazes maturing in the range of cones 4 to 5. Because it was found to be a strong flux, strontia was used in combination with other fluxes in a group of leadless glazes and in conjunction with lead in glazes of low lead content (0.15 molecule and less). The feasibility of lowering, or eliminating entirely, the lead content of a glaze by the use of strontia could be studied in this way.

Leadless or nearly leadless glazes would be desirable for dinnerware, but they have not had much commercial use chiefly because of their inferiority in gloss and surface properties. Lithia, even in small amounts, has been found to increase the gloss measurably. For this reason and because it is a strong flux, lithia was used along with strontia in this group of glazes.

The molecular formulas of some of the better laboratory glazes which were fired in commercial kilns are given in Table V. All were made with special frits and prepared, fired, and tested in the same manner as the preceding series of glazes.

TABLE V

MOLECULAR FORMULAS OF EXPERIMENTAL GLAZES

	Leadless		Low lead		
Glaze No.	5	6	7	8	9
Na_2O	0.13	0.14	0.18	0.13	0.13
K_2O	0.07	0.04	0.07	0.02	0.04
Li_2O	0.05	0.10		0.10	0.09
CaO	0.45	0.27	0.19	0.35	0.25
SrO	0.25	0.31	0.41	0.20	0.29
MgO	0.05	0.09		0.10	0.08
BaO		0.05			0.05
PbO			0.15	0.10	0.07
Al_2O_3	0.28	0.26	0.27	0.28	0.26
SiO_2	2.80	2.70	2.80	2.70	2.70
B_2O_3	0.28	0.36	0.31	0.25	0.36

TABLE VI

PHYSICAL PROPERTIES OF EXPERIMENTAL GLAZES

Glaze No.	5	6	7	8	9
Ring test (compression, mm.)	0.097	0.050	0.143	0.093	0.110
Thermal shock (No. out of 12 passing 5 cycles)	9	12	12	11	12
Autoclave (No. out of 12 passing 1 cycle)	11	11	11	11	11
Modulus of rupture (lb./sq. in.)	4906	4610	4707	5443	5078

In physical properties (Table VI) as well as in surface qualities, this group of glazes proved to be quite satisfactory. The two leadless glazes, although slightly inferior to that developed by the SrO replacement of the PbO in the base glaze, were nevertheless of excellent appearance. Among the low-lead group, No. 8 in particular was superior in optical and physical properties, comparing favorably in every respect with a glaze of normal lead content. This series was merely a preliminary study, but it is felt that glazes of this type have such possibilities as to deserve further investigation.

V. Discussion

This investigation was limited to a particular glaze field, but it indicates the behavior of strontia in other glazes. Desirable properties, such as greater elasticity, better surface qualities, and a longer and lower fusion range, may be obtained by increasing the number of basic oxides in a given glaze. Strontia should therefore be a desirable glaze addition. With its use, however, would come other distinctive advantages as manifested by the data already presented. By virtue of its strong fluxing power, strontia would aid in depressing the fusion temperature and at the same time effectively increase fluidity. Where underglaze colors are employed, the use of SrO in place of ZnO would not only prevent destruction of the colors but also greatly improve fluidity. Complete substitution of strontia for lime would be impractical, but partial replacement would bring compensating advantages in greater fluidity and lower fusion temperature. Complete replacement of the lead oxide in a glaze would not be entirely satisfactory, but a reduction of its content would be possible with additions of SrO, at the same time retaining desired glaze properties. Because strontium salts are nontoxic, this substitution would reduce the health hazard of the lead and acid solubility of the glaze would also be measurably reduced.

Like other glaze oxides, the greatest effectiveness of strontia can be obtained by including in it the frit. The insolubility of strontium carbonate permits its use in the mill addition with good results but introducing at least part of it in the frit greatly increases its influence in depressing the fusion temperature and increasing fluidity.

VI. Summary

(1) A base-glaze molecular replacement of PbO with SrO raised the deformation temperature, fused viscosity, thermal expansion, and water solubility but lowered acid solubility.

(2) Replacement of the ZnO with SrO slightly raised the deformation temperature, thermal expansion, and acid solubility, and lowered the fused viscosity and water solubility.

(3) Replacement of the CaO with SrO raised the deformation temperature slightly in the raw glaze but lowered it in the fritted batches, lowered fused viscosity and water solubility, and increased the acid solubility. There was little change in thermal expansion.

(4) Molecular replacement of the CaO in a soda-lime glass with SrO increased thermal expansion and lowered fused viscosity and deformation temperature.

(5) Weight replacement of the CaO in a soda-lime glass with SrO lowered fused viscosity and deformation temperature and made little change in thermal expansion.

(6) Glaze stress, modulus of rupture, autoclave, and thermal-shock tests showed good fritting properties in all of the glazes.

(7) Laboratory tests indicated strontia to be particularly effective in leadless, low-lead, and low-maturing glazes.

Acknowledgment

The writer wishes to acknowledge his indebtedness to his adviser, G. A. Bole; to the Foote Mineral Company, sponsor of the project; and to L. H. Brown of the Hall China Company, J. W. Hepplewhite of the Edwin M. Knowles China Company, and Edward Schramm of the Onondaga Pottery Company for their kind cooperation in the plant tests.

Engineering Experiment Station
The Ohio State University
Columbus, Ohio

SOME FACTORS AFFECTING THE P.C.E. OF SILICA FIRE CLAY*

By Raymond E. Birch and Morris P. Hall

Abstract

A study was made of the factors affecting the pyrometric cone equivalent (P.C.E.) of silica fire clay made of ganister, clay, and silica-brick culls. These factors include grind, mix proportions, and quality of raw materials.

I. Introduction

The bonding mortars used with silica brick are most commonly silica fire clays, which are prepared mixtures of clay, silica-brick culls, and ganister. For the clay constituent of silica fire clay, the siliceous kaolins of the Nittany valley in Pennsylvania are widely used. In normal practice, the ratio of ganister to culls is kept constant and the percentage of kaolinitic clay is varied from 20 to 40% to meet the requirements of service.

Table I

Chemical Analysis of Raw Materials

	Mixture of ganister and culls (%)	Clay (%)
Silica (SiO_2)	96.6	62.5
Alumina (Al_2O_3)	1.0	25.8
Titania (TiO_2)	0.1	1.1
Iron oxide (Fe_2O_3)	0.5	0.5
Lime (CaO)	1.5	0.1
Magnesia (MgO)	0.1	0.5
Alkalis ($Na_2O + K_2O$)	0.1	1.6
Ignition loss	0.1	8.0
P.C.E.	32	30–31

Close control of the mix is needed because of the marked influence of clay content on refractoriness and workability. At best, silica fire clays have a short working or trowelling period. Workability can be improved by increasing the clay content, but this unfortunately also lowers refractoriness. The present paper gives some of the control data which have been useful in guiding the manufacture of a commercial silica fire clay.

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Refractories Division). Received April 10, 1944.

Refractoriness was measured by the A.S.T.M. standard method (C 24–42) of test for P.C.E. (pyrometric cone equivalent). It is important to remember in this connection, that the P.C.E. method specifies that silica fire clays shall be tested as received, without grinding or other treatment. Some of the conclusions of the writers would not hold if the samples, instead, were ground to pass 65-mesh before the test cones were prepared.

II. Raw Materials

The chemical analyses of Table I may be considered typical of the raw materials used in this study. The same mixture of ganister and culls was used throughout.

III. Effect of Fineness of Grind

To determine the effect of fineness of grind on the P.C.E., a mixture of 27.5% clay and 72.5% ganister plus culls was made up in two base grinds, one starting on 28-mesh and the other on 48-mesh. These are grinds A and F in Table II. Neither represents an extreme grind since each was made to a specification on which thousands of tons of silica fire clay have been shipped, and both might reasonably be submitted on the same specification.

As shown in Table II, silica fire clay of grinds A and F gave P.C.E. values of 29–30 and 23, respectively. The two-screen increase in fineness thus lowered the P.C.E. by four and one-half cones in the standard series.

To throw more light on this subject, samples of grinds A and F, the two end members, were blended in 20% increments. The P.C.E. values of these mixtures and their calculated screen analyses are also shown in Table II.

While these data indicate that control of grind is an effective means of increasing the P.C.E. so that a given

Table II

Effect of Percentage Fineness of Grind on P.C.E.

Screen analysis	A	B	C	D	E	F
		80A 20F	60A 40F	40A 60F	20A 80F	
	Fineness of grind (%)					
Pass 20-on 28-mesh	2 2	2 2	1 1	1 1	Trace	
" 28 " 35 "	12	9	7	5	3	Trace
" 35 " 48 "	12	10	8	6	4	2
" 48 " 65 "	12 36	12 31	12 27	10 21	10 17	10 12
" 65 " 100 "	8	9	10	11	12	13
" 100 " 150 "	9	10	11	11	12	13
" 150 " 200 "	7	7	7	8	8	8
" 200	38 62	41 67	4 72	48 78	51 83	54 88
P.C.E.	29–30	29	28–29	27	23–26	23

specification may be met, it is doubtful whether the actual benefits to the user are of great value. The heating time in a P.C.E. test of a silica fire clay is about 90 minutes. Variation in grain size, which is one factor affecting ceramic fusions, is more noticeable in this brief time at high temperatures than in a more extended period. If sufficient time were provided for reaching equilibrium, there would be no difference in the amount of fusion at a given temperature. The coarser grinds, which in these tests gave the higher values of P.C.E., nevertheless should offer some advantage in service since the approach toward equilibrium will be retarded by the lack of homogeneity.

One of the factors that prevents the full use of grind in controlling the P.C.E. of silica fire clay is the impairment of trowelling properties, which is observed when the grind is coarse. Masons prefer a smooth-working mortar and are quick to protest if a silica fire clay seems more gritty than usual.

Tests were run to determine the working time for each of the six grinds. When mixed with 36 to 38% of water (dry basis) to give a trowelling consistency, there was no appreciable difference in the time during which the various samples could be freely trowelled on a clean dry silica brick.

An increase in the coarseness of silica fire clay has an adverse effect on its ability to stay in suspension, but all of the mixes of Table II had satisfactory suspension properties.

IV. Effect of Mix Proportions

To determine the effect of clay content on the P.C.E., six proportions of clay, from 15 to 40% each, were added to the base mix of ganister and culls. To minimize the effect of grind as a variable, the two end members in the series were made to approximately the same screen analysis (see Table III) and all other mixes were made by blending these two.

The results of this series of tests, as shown in Table III reveal that each increase in clay from 15 to 40% decreased the P.C.E. It is considered that the reduction in refractoriness is due mainly to the increase in alumina as more clay is supplied.

TABLE III

EFFECT OF CLAY CONTENT ON P.C.E. OF SILICA FIRE CLAY

	Clay (%)	Estimated Al_2O_3 (%) calcined basis	P.C.E.
G	15	4.8	29–30
H	20	6.1	28–29
I	25	7.3	27–28
J	30	8.7	26
K	35	10.0	23–26
L	40	11.3	23

	Screen analyses of end mixes (%)			
	G (15% clay)		L (40% clay)	
Pass 20- on 35-mesh	Trace		1	
" 35 " 48 "	6		10	
" 48 " 65 "	12	18	9	20
" 65 " 100 "	17		12	
" 100 " 150 "	12		8	
" 150 " 200 "	9		7	
Pass 200	44	82	53	80

V. Effect of Clay Quality (Table IV)

The Pennsylvania kaolins vary in silica content within rather wide limits and therefore in refractoriness. All of the foregoing tests were run with clay having an alumina content of about 25.8% (SiO_2, 62.5%) and a P.C.E. of 30–31. To determine the importance of clay quality, a silica fire-clay mix of 27.5% clay and 72.5% ganister plus culls was prepared with the cone 30–31 clay and with another clay sample having an alumina content of about 17.1% (SiO_2, 72.7%) but with a P.C.E. of only 28. A single sample of ganister and culls was used, and it was carefully split to insure that the grind of both mixes was the same. The resulting silica fire clays showed P.C.E. values of 26–27 and 29, respectively, that is, the less refractory and more siliceous of the two clays gave the silica fire clay a higher refractoriness. This result was momentarily surprising, but it need not have been because the less refractory clay had a lower alumina content and its substitution for the more refractory bond clay would decrease alumina and have the same effect as decreasing the clay content.

TABLE IV

EFFECT OF CLAY QUALITY ON P.C.E. OF SILICA FIRE CLAY

Clay properties	Sample A	Sample B
Chemical analysis (crude basis)		
Silica (%)	62.5	72.7
Alumina estimated (%)	25.8	17.1
Ignition loss (%)	8.0	6.1
P.C.E.	30–31	28
Silica fire clay containing 27.5% of these clays		
Chemical analysis (calcined basis, estimated)		
Silica (%)	89.3	92.1
Alumina (%)	8.0	5.6
P.C.E.	26–27	29

VI. Conclusions

In silica fire clay made of siliceous kaolinitic clay, ganister, and silica-brick culls, the P.C.E. was found to be highly responsive to changes in grind, the coarser grinds giving a higher P.C.E.

The P.C.E. was lowered by increases in clay content from 15 to 40% clay.

Of two similar clays having P.C.E. values of 30–31 and 28, the latter gave the more refractory product when blended with ganister and silica-brick bats because it was less aluminous.

Any reference to phase-equilibrium data could only be for the purpose of pointing out that little guidance can be had from their use in connection with studies of this type. The composition of lowest melting temperature (eutectic) in the system Al_2O_3–SiO_2 is 94.5% SiO_2, 5.5% Al_2O_3, but the P.C.E. of these silica fire clays was still falling when the last increment of clay addition (40% total) brought the alumina content to 11.3%. Since the clay itself, however, had a P.C.E. of 30–31, it is obvious that a somewhat greater percentage would have reversed the trend and would have increased the P.C.E. The nature of the P.C.E. end point and its dependence on heating rate and on the

viscosity of the liquid developed largely eliminate the usefulness of phase-equilibrium data for P.C.E. studies, which are not dependent on these factors. Phase-equilibrium data, furthermore, require homogeneity and the attainment of equilibrium, while the foregoing data showing the dependence of P.C.E. on grind are proof that neither of these conditions is attained when silica fire clays are tested by the standard method for P.C.E. It is true, however, that phase-equilibrium data show that small amounts of CaO, as present in these mixes, result in an appreciable shift in composition of the least refractory mix toward the more aluminous end of the series.

References

1. E. N. McGee, "Silica Cement," *Jour. Amer. Ceram. Soc.*, **6** [8] 896–903 (1923).
2. Sandford S. Cole, "Effect of Size of Grain upon Properties of Silica Cement," *ibid.*, **10** [8] 644–50 (1927).
3. Sandford S. Cole, "Variations in Pyrometric Cone Equivalents of Silica Cements and Fire Clays," *ibid.*, **11** [11] 854–57 (1928).
4. W. D. Keller, "P.C.E. of Coarse-Grained Refractories," *Ceram. Age*, **18** [1] 18–19 (1931); *Ceram. Abs.*, **10** [11] 783 (1931).

Acknowledgment

The P.C.E. tests were carried out by C. F. Bruce at Hays Laboratory.

Research Department
Harbison-Walker Refractories Company
Pittsburgh, Pennsylvania

LIGHTWEIGHT SUPERDUTY KYANITE-TOPAZ REFRACTORY*

By W. W. Galbreath, Jr., T. N. McVay, and Dan Allen†

Abstract

Standard-size 9-in. brick with a weight of 5 lb. were successfully processed. Some of these brick had linear shrinkages of less than 1% in the A.S.T.M. load test at 1450°C. and less than 2% volume shrinkage in the 1600°C. A.S.T.M. reheat test. The pyrometric cone equivalent was 37 or above.

I. Introduction

The object of this investigation was to produce a standard-size firebrick that would weigh between 4.5 and 6 lb. and would meet the A.S.T.M. specifications and, preferably, the more severe Navy Department reheat specifications‡; both specifications require a pyrometric cone equivalent above cone 33. Because of their high porosity, such lightweight refractories have relatively low thermal conductivity. The brick, however, were not designed primarily for their insulating value but for service conditions where the saving of weight is an important factor.

II. Materials and Method of Processing

Combinations of calcined domestic kyanite with raw topaz were used because previous investigations[1] have shown that these materials produce excellent refractories and that raw topaz has marked bonding action at elevated temperatures. Carbonaceous materials, such as charkets (briquetted charcoal), petroleum coke, sawdust, and anthracite, were incorporated in the mixtures. The carbon and carbon compounds in the additions were oxidized in firing, producing a porous lightweight body. The most satisfactory results, however, were obtained in processing with anthracite.

A high clay content, such as is necessary for the production of brick by the stiff-mud process, tends to reduce the constancy of volume at high temperatures either by shrinkage or by overfiring of the bond clay. All standard-size experimental brick, consequently, were made by the power press, and the clay content was only 10%.

III. Preliminary Investigations

Three series of lightweight refractory compositions were prepared, and the compositions are shown in Table I. The batches were mixed with the proper amount of water and 2% of an organic binder, and small test pieces, 2 by 1 by 1 in. in size, were pressed at 7500 lb. per sq. in. After drying, the specimens were

* Received June 8, 1944. Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior, and under a general cooperative agreement with the Tennessee Valley Authority.

† The authors are, respectively, junior ceramic engineer, Electrotechnical Laboratory; senior mineralogist, Southern Experiment Station, in charge of the refractories section at Norris, Tenn.; and physical science aide, Electrotechnical Laboratory, U. S. Bureau of Mines, Norris, Tenn.

‡ The A.S.T.M. specifications (C27–40T) for superduty fire-clay brick require that there shall be not more than 1% linear shrinkage in the permanent linear-change test, Schedule C (1600°C., 5 hours); the Navy Department specifications (32B 2c) state that the permanent volume change after reheating at 2912°F. (1600°C.) for 5 hours shall be not more than +3% or −1%.

[1] T. N. McVay, W. W. Galbreath, Jr., and Dan Allen, "Raw Topaz as a High-Temperature Bond for Domestic Kyanite." Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Refractories Division); to be published in an early issue of this *Journal*.

oxidized and then fired for 4 hours at 1500°C. The linear change in firing did not exceed 0.6% for any of the compositions. The porosities and densities (expressed in pounds per cubic foot) have been plotted and are shown in Figs. 1 to 6.

The results showed that, for equal weight additions, charkets produced a fired refractory with a lower weight per cubic foot than either petroleum coke or anthracite, but petroleum coke and anthracite gave a better structure than charkets. Petroleum coke was more difficult to oxidize than the other materials. No difficulties were encountered in the use of anthracite. Two series of compositions were made which contained both soft- and hard-wood sawdust. On account of the elasticity of the sawdust, such compositions did not press satisfactorily.

The ash content of petroleum coke was 0.9%, charkets 5.7%, and anthracite 9.9%; for equal weight additions of the three carbonaceous materials, therefore, anthracite introduced the most ash. The pyrometric cone equivalent of the anthracite ash, however, was 31 to 32, whereas the fusion point of the charket ash was very low.

Standard-size brick were pressed, which contained varying proportions of charkets, petroleum coke, sawdust, and anthracite, respectively. The structure of the fired brick containing sawdust was very poor. The brick containing charkets not only had a poor structure, but the shrinkage in the reheat tests was excessive. Petroleum coke was eliminated from consideration because of the excessive length of time needed for oxidation. All subsequent efforts were directed toward the use of anthracite for decreasing the weight.

IV. Processing of Standard-Size Brick

Table II gives the composition of standard-size lightweight brick and Table III, their properties before and after reheat. Brick of this series were pressed at 7400 lb. per sq. in. After oxidation, they were fired 4 hours at 1500°C.

The reheat tests at 1600°C. were conducted according to A.S.T.M. specifications C113–36 Schedule C, and the data are shown in Table III.

To complete the oxidation of the anthracite in the standard-size brick during the firing in the electric Globar kiln, it was necessary to introduce air during the oxidation period. This resulted in good oxidation of all subsequent brick.

Composition A was selected as a basis for subsequent experimental work. Brick made from this mixture had a good structure, the volume shrinkage in the preheat was low, and the weight of standard-size brick was below 5 lb. The −35-mesh kyanite, moreover, costs less than the −100-mesh product. A satisfactory bond was produced with 20% topaz, and the volatiles from this amount of topaz when diluted with the other flue gases should not cause any health hazards. As raw topaz decreases the spalling resistance, there is an advantage in keeping the topaz content at the minimum amount that will produce a satisfactory bond.

TABLE I

LIGHTWEIGHT REFRACTORY COMPOSITIONS (%)

Fig. No.	Per cent	Mesh	Material
		Series C, petroleum-coke additions	
1-A	80	−100	Calcined Va. kyanite
	20	−100	Raw S. C. topaz
	With	−14	Petroleum-coke additions
2-B	70	−100	Calcined Va. kyanite
	20	−100	Raw topaz
	10		Edgar plastic kaolin
	With	−14	Petroleum-coke additions
		Series I, charket additions	
3-A	70	−100	Calcined Va. kyanite
	20	−100	Raw topaz
	10		Edgar plastic kaolin
	With	−8	Charket additions
4-B	60	−100	Calcined Va. kyanite
	30	−100	Raw topaz
	10		Edgar plastic kaolin
	With	−8	Charket additions
		Series K, anthracite additions	
5-A	70	−100	Calcined Va. kyanite
	20	−100	Raw topaz
	10		Edgar plastic kaolin
	With	−8	Anthracite
6-B	60	−100	Calcined Va. kyanite
	30	−100	Raw topaz
	10		Edgar plastic kaolin
	With	−8	Anthracite

TABLE II

COMPOSITION OF LIGHTWEIGHT REFRACTORY BRICK (10% Edgar plastic kaolin added) (%)

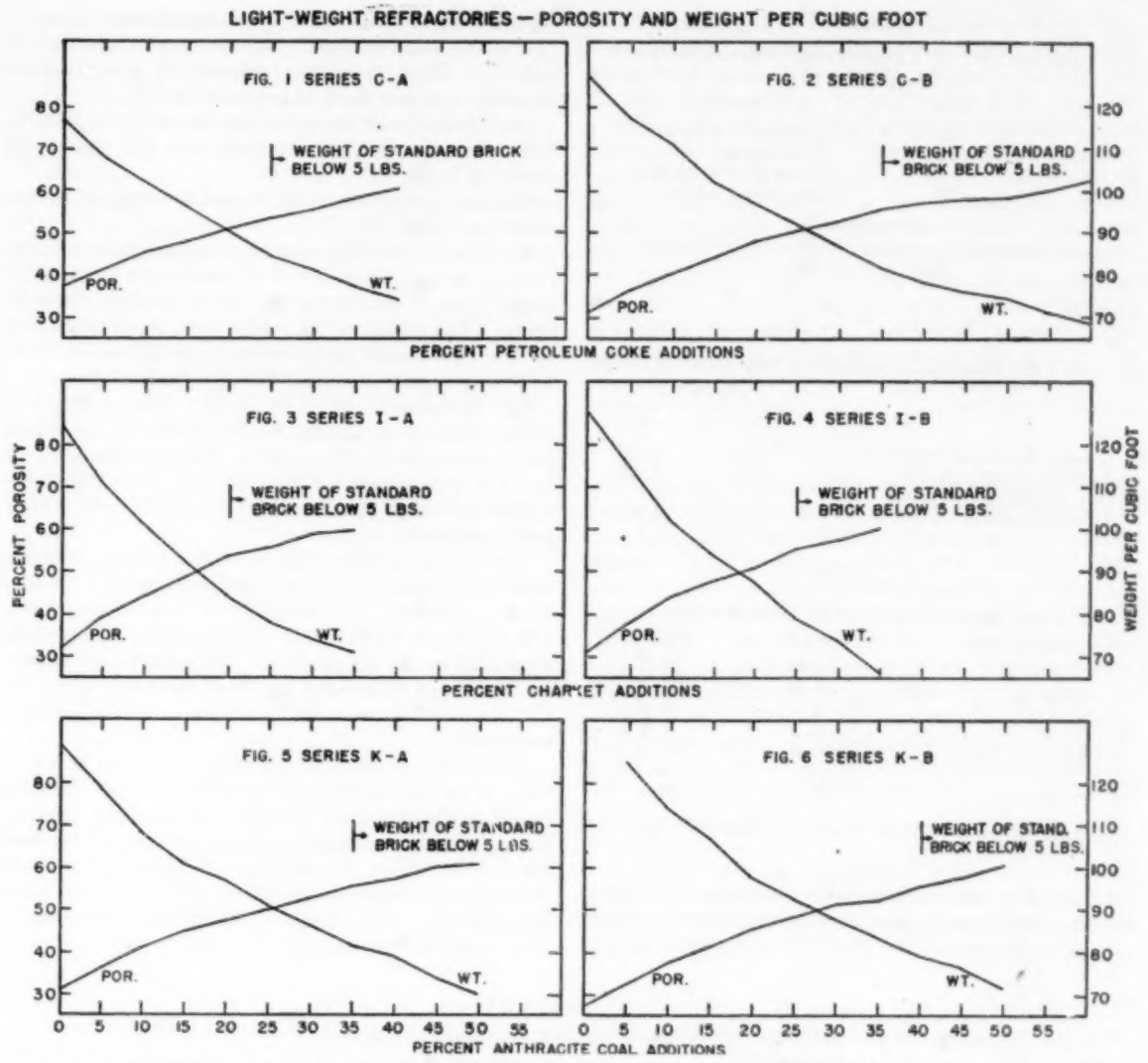
Bur. Mines brick No.	Calcined Va. kyanite −35 mesh	Calcined Va. kyanite −100 mesh	Raw topaz −100 mesh	Anthracite −8 mesh
A1–A2	70		20	35
B1	70		20	40
C1	60		30	35
D1	60		30	40
E1–E2		70	20	35
F1–F2		70	20	40
G1–G2		60	30	35
H1–H2		60	30	40

TABLE III

PROPERTIES OF STANDARD-SIZE LIGHTWEIGHT REFRACTORY BRICK BEFORE AND AFTER REHEAT TO 1600°C.

Bur. Mines brick No.	Porosity (%) Before reheat	Porosity (%) After reheat	Weight (lb.) Before reheat	Weight (lb.) After reheat	Shrinkage (%) Volume	Shrinkage (%) Linear
A1*	54.5	55.0	4.8	4.85	2.3	0.6
A2	55.8	54.3	4.8	4.90	3.2	0.9
B1*	50.7	55.0	4.9	5.0	3.2	0.4
C1*	47.7	50.8	5.2	5.1	2.7	0.4
D1*	53.8	55.0	4.8	4.8	3.2	1.1
E1	56.0	54.3	4.8	4.9	3.9	1.4
E2*	53.2	54.3	4.9	4.9	2.9	0.7
F1*	57.8	56.6	4.6	4.7	3.3	0.9
F2*	55.0	55.5	4.7	4.8	3.4	1.0
G1	54.7	53.8	4.9	5.0	3.5	1.2
G2*	53.3	53.1	5.0	5.05	4.7	1.3
H1	57.4	55.7	4.6	4.8	3.7	1.4
H2	56.8	55.6	4.6	4.7	3.7	1.0

* These brick showed considerable loss of weight in the reheat test which indicates that oxidation of the anthracite was not complete.



FIGS. 1–6.—Porosity and density of standard lightweight refractories with additions of petroleum coke, charkets, and anthracite coal, respectively.

A series was made of composition A but with varying mesh sizes of the anthracite. Within the limits of the experimental data, however, the mesh size of the anthracite had no appreciable effect on the properties of the refractories. Because there is some advantage from the standpoint of low-heat conductivity in having small-size pores, −35-mesh anthracite was used in all subsequent experiments. Table IV shows results of reheat tests on five brick of composition Z, using −35-mesh anthracite (see Table V). All brick were preheated 4 hours at 1500°C.

The results in Table IV showed that a preheat of 4 hours at 1500°C. was not sufficient to reduce the volume shrinkage in the reheat test to 1% or less.

A study was made of the effect of forming pressure on the structure of the refractories, and it was found that a pressure of 5000 lb. per sq. in. produced a brick with fewer press cracks than a pressure of 7400 lb. per sq. in. Within these limits, moreover, pressure had little effect on volume shrinkage in the reheat tests. A pressure of 5000 lb. per sq. in., therefore, was used in all subsequent experiments.

TABLE IV

PROPERTIES OF STANDARD-SIZE LIGHTWEIGHT REFRACTORY BRICK BEFORE AND AFTER REHEAT AT 1600°C.

Bur. Mines Brick No.	Porosity (%)		Weight (lb.)		Shrinkage (%)	
	Before reheat	After reheat	Before reheat	After reheat	Volume	Linear
Z1	58.5	57.8	4.5	4.6	2.9	1.1
Z2	56.3	55.2	4.8	4.9	3.4	0.9
Z3	55.6	53.9	4.8	5.0	4.5	1.8
Z4	56.5	54.6	4.7	5.0	5.3	1.9
Z5	56.6	54.7	4.8	5.0	4.2	1.2
Avg.	56.7	55.2	4.7	4.9	4.1	1.4
Z5*	54.7	54.5	5.0	5.0	1.0	0.5

* The first reheat at 1600°C. for 5 hours was considered the preheat for this test.

TABLE V

COMPOSITION OF LIGHTWEIGHT REFRACTORIES

Composition N

(%)	Mesh	Material
70	−35	Calcined Va. kyanite
20	−100	Raw topaz
10		Edgar plastic kaolin
25	−35	Anthracite added

Composition Z

Same composition except for 35% of −35-mesh anthracite added.

TABLE VI

REHEAT TEST RESULTS (COMMERCIAL LABORATORY TESTS)

	Brick No.	
	N1	Z6
Linear shrinkage (%)	0.14	0.29
Volume shrinkage (%)	0.91	1.32
Wt. standard-size brick before reheat (lb.)	5.42	4.98

TABLE VII

ANALYSES OF LIGHTWEIGHT REFRACTORIES

Composition*	Brick N	Brick Z
Al_2O_3	58.4	55.8
SiO_2	36.0	38.9
Fe_2O_3	2.1	2.3
TiO_2	1.7	1.7
Ignition loss	0.6	0.4
Total	98.8	99.1

* Analyses made by H. R. Shell, assistant chemist.

In order to determine whether experimental lightweight refractories made at Norris would have a reheat volume shrinkage of less than 1% when preheated at 1600°C., eight brick each of compositions N and Z (Table V) were pressed, oxidized, and preheated at 1200°C. They were then shipped to a commercial manufacturer and fired 10 hours at 1600°C.

One brick of each composition was given the 1600°C. reheat test by the manufacturer and the results are shown in Table VI.

Chemical analyses of the N and Z compositions are shown in Table VII.

To have more brick available for experimental purposes, a second shipment of 40 brick each of compositions N and Z was forwarded to the manufacturer for firing The results of the reheat tests on all brick fired by the commercial manufacturer are shown in Table VIII in comparison with commercial refractories.

(A) Designation of Test Brick: The commercial refractories are designated by the prefix C; the others are experimental refractories. Refractories CI, CJ, and CK were superduty flint fire-clay brick, CL was a lightweight high-alumina brick, and CM was a high-grade refractory insulator.

The results in Table VIII show that the experimental brick were superior to the heavier superduty fire-clay brick in constancy of volume at elevated temperatures. The CL brick (lightweight high alumina) had a slight expansion in the reheat test. The reheat data showed no significant differences between the two experimental compositions or between the two methods of heat-treatment.

All of the commercial superduty fire-clay brick in these tests had shrinkages in excess of that allowable by either the A.S.T.M. or Navy Department specifications. As the commercial refractories presumably meet the specifications, the Bureau of Mines reheat tests probably are more severe than those made in other laboratories. The furnaces at Norris are carbon-resistance electric furnaces and operate under strongly

TABLE VIII

PROPERTIES OF STANDARD-SIZE REFRACTORY BRICK BEFORE AND AFTER REHEAT TO 1600°C.

Brick No.	Porosity (%)		Weight (lb.)		Shrinkage (%)	
	Before reheat	After reheat	Before reheat	After reheat	Volume	Linear
			Bur. Mines test brick			
N2*	49.3	49.2	5.5	5.6	1.3	0.5
N3†	50.6	50.9	5.35	5.4	1.1	0.2
N4†	50.3	49.7	5.4	5.5	1.8	0.6
N5‡	52.0	51.1	5.25	5.3	2.0	0.7
N6‡	52.1	50.9	5.20	5.4	3.7	1.3
Z7*	53.4	53.2	5.1	5.1	1.5	1.1
Z8‡	56.3	56.0	4.7	4.8	2.0	0.3
Z9‡	57.0	56.7	4.7	4.8	2.8	0.0
			Commercial test brick			
CI–1	11.0	3.5	8.6	9.0	4.8	2.3
CJ–1	13.0	4.4	8.5	9.0	5.8	3.3
CJ–2	13.9	2.8	8.5	9.0	6.7	3.4
CK–1	14.7	7.9	8.5	9.0	5.8	3.0
CK–2	14.8	7.8	8.5	9.0	6.2	3.0
CL–1	64.2	64.2	4.5	4.4	−1.3	−0.3
CL–2	64.4	64.4	4.5	4.4	−1.7	−0.3
CM–1			3.3	3.6	7.8	3.9
CM–2			3.3	3.5	2.8	1.6

* First lot fired by commercial manufacturer 10 hr. at 1600°C.
† Second lot fired by commercial manufacturer 10 hr. at 1600°C.
‡ Fired in a commercial tunnel kiln at cones 20 to 26.

reducing conditions; they may give a more severe heat-treatment than oil- or gas-fired furnaces.

Constant-temperature (A.S.T.M. C16–39T, schedule 3) and variable-temperature load tests[1] were also made on the experimental and some of the commercial refractories. The results of the A.S.T.M. tests are given in Table IX.

The results show that the experimental brick had excellent load resistance at high temperatures and were superior to the commercial superduty fire-clay brick CI, CJ, and CK.

TABLE IX

CONSTANT-TEMPERATURE LOAD-TEST RESULTS
(A.S.T.M. Test at 1450°C.)

Brick No.	Wt. standard-size brick (lb.)	Linear shrinkage (%)
	Bur. Mines test brick	
N7*	5.3	2.1
N8*	5.3	0.3
N9†	5.4	0.7
N10†	5.3	1.0
Z10†	4.7	0.7
Z11†	4.6	1.6
	Commercial test brick	
CI–2	8.5	2.5
CJ–3	8.5	4.3
CJ–4	8.5	5.8
CK–3	8.5	5.6
CK–4	8.5	6.3
CL–3	4.6	1.0
CL–4	4.6	1.0
CM–3	3.3	3.2
CM–4	3.3	3.1

* Fired by commercial manufacturer 10 hr. at 1600°C.
† Fired in commercial tunnel kiln at cones 20 to 26.

The data for the variable-temperature load tests are given in Table X.

The brick given in Table X are the same as have previously been described, except for CN–1 and CN–2, which were made from a body containing a large percentage of thoroughly calcined kaolin grog. The linear-shrinkage data for the various refractories are not comparable because the maximum temperatures were not constant. The temperatures of the 45-degree tangent indicate that, with one exception, the experimental Bureau of Mines brick were more resistant to initial and rapid shrinkage than the other refractories included in the table. The N brick are only slightly superior to those of CL composition, and the differences lie within the range of experimental error. The thermal expansion of the CL brick is higher than that of the experimental kyanite-topaz refractories.

V. Conclusions

The results of the study show that refractories made from N and Z compositions meet the A.S.T.M. shrinkage requirements in the reheat tests, and the results obtained in a commercial laboratory indicate that brick of N composition fired 10 hours at 1600°C. will meet the more severe Navy Department specifications. The results of the reheat and both types of load tests show that the experimental brick are superior to the 8.5-lb. commercial superduty, flint fire-clay brick in constancy of volume as well as in resistance to load at high temperatures. The lightweight, high-alumina CL brick have excellent load resistance and constancy of volume when heated at 1600°C. The insulating refractory CM is also exceptionally satisfactory considering its low density.

The pyrometric cone equivalent of the N and Z compositions is cone 37 or above, which is much higher than either the A.S.T.M. or Navy Department requirements.

TABLE X

VARIABLE-TEMPERATURE LOAD-TEST RESULTS

Brick No.	Wt. standard brick before test (lb.)	Temp. range of constant max. expansion (°C.)	Temp. 45° tangent (°C.)	Max. hot expansion (%)	Max. furnace temp., (°C.)	Linear shrinkage (%)
			Bur. Mines test brick			
N11*	5.4	1020–1435	1470	0.60	1550	1.1
N12*	5.4	1100–1430	1475	0.60	1560	1.2
N13†	5.3	1120–1440	1460	0.55	1550	1.4
N14†	5.3	1040–1470	1500	0.65	1555	0.0
Z12†	4.7	940–1270	1360	0.75	1550	4.7
Z13†	4.7	1020–1420	1425	0.55	1550	5.5
			Commercial test brick			
CI–3	8.6	1320	1400	0.40	1500	2.3
CI–4	8.6	1030–1280	1350	0.45	1560	6.3
CJ–5	8.4	1275	1295	0.50	1450	2.5
CJ–6	8.6	930–1200	1260	0.55	1470	3.8
CK–5	8.4	930–1190	1245	0.60	1450	4.7
CK–6	8.5	950–1210	1200	0.67	1455	4.8
CN–1	7.9	1050–1290	1335	0.80	1500	3.2
CN–2	7.8	800–1220	1350	0.75	1500	2.8
CL–5	4.5	1120–1425	1430	0.90	1600	2.5
CL–6	4.6	1160–1430	1485	0.95	1600	3.2
CM–5	3.3	800–1210	1300	0.40	1520	5.3
CM–6	3.3	800–1155	N.d.	0.45	1545	4.2

* Fired by a commercial manufacturer 10 hours at 1600°C.
† Fired in a commercial tunnel kiln at cones 20 to 26.

Acknowledgment

The writers wish to thank the A. P. Green Fire Brick Company, the Harbison-Walker Refractories Company, the Babcock & Wilcox Company, the Carborundum Company, and the United Feldspar & Minerals Corporation for their cooperation. They are also indebted to Hewitt Wilson for reviewing the manuscript and for his suggestions during the course of the investigation.

THE ELECTROTECHNICAL LABORATORY
U. S. BUREAU OF MINES
NORRIS, TENNESSEE

HIGH-ALUMINA CLAYS OF PULASKI AND SALINE COUNTIES, ARKANSAS*

BY JOSHUA I. TRACEY, JR.

ABSTRACT

Extensive deposits of kaolinitic clay and closely associated bauxite occur in Pulaski and Saline counties, Arkansas, as products of early Cenozoic weathering of nepheline syenite. The clays of the bauxite-kaolin deposits normally contain more than 35% of alumina. Siderite is the principal impurity. The deposits for the most part are buried beneath sediments of Wilcox age or younger, but the overburden is thin or absent near outcrops of syenite. Deposits beneath overburden that does not exceed 50 feet in thickness probably total more than 100 million tons.

I. Introduction

Extensive deposits of high-alumina clays, consisting of hydrous aluminum silicates, are found in Pulaski and Saline counties, Arkansas. They are associated with and closely related to the better-known deposits of bauxite.

Field parties of the U. S. Geological Survey and the U. S. Bureau of Mines have collected much information concerning the occurrence and nature of these clays. The information has been derived in part from the geologic logs of several thousand holes drilled for the Bureau of Mines during the course of the investigation of the bauxite deposits, in part from chemical analyses of samples of the cores taken, and in part from drilling data and analyses belonging to mining companies in the area. Complete reports on certain individual deposits of bauxite and clay are to be released in the future as Bureau of Mines War Minerals Reports. Meanwhile, because the clays must be of interest to the refractory-clay industry, this paper is offered as a preliminary and informal discussion of their character and geologic distribution.

II. Location and Description of Deposits

The clays described here occur in Pulaski and Saline counties, which lie at the very center of Arkansas. Together with bauxite, they are found in an area roughly 25 miles long and 7 miles wide, extending southwestward from the city of Little Rock, Pulaski County, to and beyond the town of Bauxite, Saline County. The country is gently rolling to hilly, with relief that hardly anywhere exceeds 150 feet. Two railroads cross the area, and spur lines lead to the main bauxite-producing localities. All parts of the district are easily accessible by hard-surfaced highways and gravel roads.

The high-alumina clay district extends along the contact of Tertiary Coastal Plains sediments with folded Paleozoic rocks. Protruding through the Paleozoic rocks and flanked by the edge of the Coastal Plains sediments are hills of nepheline syenite. The bodies of bauxite and high-alumina clays lie along the sides of the nepheline-syenite hills and for the most part are buried by later Coastal Plains sediments.

The high-alumina clay encloses many lenticular deposits of bauxite, which grade both laterally and vertically through bauxitic clay into kaolinitic clay. The transition is more abrupt in the vertical than in the horizontal direction. The bodies of high-alumina clay and bauxite, where present, together make up what will be referred to as the "bauxite-kaolin zone." This zone attains a maximum thickness of more than 80 feet, though typical deposits are not more than 50 or 60 feet thick.

In color, texture, and composition, the materials present in the bauxite-kaolin zone show great diversity although a normal or typical sequence can be outlined. Uppermost in the bauxite-kaolin zone is a light-gray or cream-colored kaolinitic clay, which is commonly somewhat carbonaceous at the top, is homogeneous in appearance, and has little or no plasticity. Where bauxite is present, the kaolinitic clay commonly grades downward rather sharply through tan bauxitic clay into firm pisolitic bauxite. At its base, the bauxite normally grades through tan bauxitic clay into brittle gray kaolinitic clay that contains fragments of bauxite and white kaolinitic clay. Normally underlying this gray clay, but in places directly beneath the

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Materials and Equipment Division). Received February 16, 1944.

Published with the permission of the Director of the U. S. Geological Survey, Department of the Interior.

TABLE I

CHEMICAL ANALYSES OF TYPICAL HIGH-ALUMINA CLAYS (%)

Sample depth	Description of clays	Al_2O_3	SiO_2	Total Fe as Fe_2O_3	TiO_2	Ignition loss	Insoluble	FeO
12.0–16.0	Gray kaolinitic	35.8	41.1	5.4	3.1	14.0	0.6	1.2
16.0–20.0	" "	38.6	42.2	1.8	2.8	13.8	0.8	0.3
20.0–24.0	" "	38.5	41.3	2.1	2.6	13.7	1.8	0.2
24.0–28.0	" "	38.1	41.3	2.4	2.8	14.3	1.1	0.2
28.0–32.0	Light-gray bauxitic	41.6	36.8	1.9	2.8	16.1	0.8	0.2
32.0–34.3	" " "	36.2	32.8	9.2	3.4	17.7	0.7	6.9
34.3–38.3	No recovery							
38.3–42.3	Light-gray bauxitic	41.6	36.4	2.6	2.0	16.7	0.7	1.2
42.3–43.5	No recovery							
43.5–48.0	Light-gray bauxitic	42.3	35.5	1.5	2.8	16.9	1.0	0.2
48.0–50.0	Tan bauxite	47.2	16.8	7.8	2.8	24.9	0.5	5.2
50.0–52.0	" "	48.8	14.2	7.1	3.4	25.7	0.8	5.1
52.0–54.5	Sideritic bauxite	32.3	9.4	26.9	3.4	27.4	0.6	24.6
54.5–56.0	No recovery							
56.0–60.0	Sideritic bauxitic	35.6	18.5	18.8	2.6	23.8	0.7	14.8
60.0–64.0	White kaolinitic	32.9	38.5	9.3	2.4	16.1	0.8	6.0
64.0–68.0	Clayey decomposed syenite	34.5	40.3	5.5	2.0	14.7	3.0	2.2
68.0–70.3	" " "	23.0	43.9	2.8	1.5	8.1	20.7	0.6

TABLE II

CHEMICAL ANALYSES OF TYPICAL HIGH-ALUMINA CLAYS (%)

Sample depth	Description of clays	Al_2O_3	SiO_2	Total Fe as Fe_2O_3	TiO_2	Ignition loss	Insoluble	FeO
56.5–59.5	Dark-gray carbonaceous	38.6	42.2	2.3	2.2	14.4	0.3	0.4
59.5–62.9	" " "	41.4	39.7	1.5	1.8	15.2	0.4	0.2
62.9–67.0	Lignite and carbonaceous (not sampled)							
67.0–70.5	Brittle gray fragmental kaolinitic	41.0	37.3	1.3	3.2	16.6	0.6	0.4
70.5–74.5	Brittle gray fragmental kaolinitic	42.9	33.8	1.2	2.8	18.3	1.0	0.2
74.5–75.5	Lignitic (not sampled)							
75.5–78.5	Light-gray bauxitic	40.5	35.4	2.3	3.2	17.7	0.9	0.2
78.5–82.5	" " "	42.3	34.4	2.0	2.8	17.0	1.5	0.4
82.5–86.5	" " "	42.4	34.6	2.2	2.8	17.2	0.8	0.2
86.5–90.5	" " "	41.8	32.5	2.0	3.6	17.8	2.3	0.3
90.5–94.5	" " "	41.7	34.7	2.9	2.6	16.9	1.2	1.2
94.5–98.5	Brittle dark-gray kaolinitic	38.0	39.7	2.0	3.1	14.9	2.3	0.5
98.5–102.5	" " " "	38.9	42.7	1.0	2.6	13.9	0.9	0.2
102.5–105.5	" " " "	37.5	42.7	1.5	3.1	13.6	1.6	0.2
105.5–110.5	Kaolinized syenite breccia	34.6	43.8	1.3	2.0	12.5	5.8	0.3
110.5–114.5	Decomposed syenite	25.1	46.4	3.3	2.0	9.4	13.8	2.2
114.5–118.5	Decomposed to fresh syenite	18.7	48.8	7.3	1.8	9.0	14.4	5.8

bauxite, is a more plastic soft white kaolinitic clay in which platy crystals of kaolinite are found.

The high-alumina clays consist chiefly of the hydrous aluminum silicate, kaolinite, or other clay minerals of the kaolinite group. Gibbsite, the trihydrate of alumina, is generally present in the upper parts of the deposits, and it becomes increasingly abundant in the transition through bauxitic clay to bauxite. Very high-grade bauxite may consist almost entirely of gibbsite.

Of the other minerals present in the deposits, all of them to be regarded as impurities, the most abundant is siderite. Crystalline siderite fills cavities in the bauxite, and the mineral also forms disseminated pellets and granular aggregates. Siderite is most abundant, on the whole, in the lower bauxitic clays, but it is abundant in other parts of some deposits, and a few deposits contain abundant siderite throughout. Aggregates and heavy concentrations of siderite are commonly of small extent. Limonite is present, probably as an oxidation and hydration product of the siderite. Biotite occurs rather sparsely in the lower white clay. Tiny grains of a titaniferous iron mineral, probably ilmenite, are disseminated in the clays. The titanium oxide content of the clays ranges from 1 to 4%, usually between 2 and 3%.

A typical clay of the bauxite-kaolin zone contains more than 35% of alumina, as compared with less than 45% of silica and less than 5% of iron oxide. In the transition through bauxitic clay to bauxite, the alumina increases and the silica decreases. In the bauxite, the alumina content normally ranges from 45 to 60% and the silica from 20% to less than 1%.

The erratic distribution of siderite causes great diversity in the iron content of the bauxite and clays, which is recorded in analyses as ferrous and ferric oxides. The total iron oxide ranges from a fraction of 1% to 50% or higher. In some high-grade bauxite deposits, the ferrous iron oxide content is prevailingly under 1% and rarely exceeds 5%. In other bauxite deposits, the ferrous iron oxide may range from 5 to 25% or more and may average over 10% for the whole

TABLE III

CHEMICAL ANALYSES OF TYPICAL HIGH-ALUMINA CLAYS (%)

Sample depth	Description of clays	Al_2O_3	SiO_2	Total Fe as Fe_2O_3	TiO_2	Ignition loss	Insoluble	FeO
34.5–38.0	Light-gray kaolinitic	35.0	37.5	8.6	2.6	15.1	1.2	4.8
38.0–43.0	Silty gray	28.0	46.2	2.1	1.8	8.6	13.3	0.9
43.0–51.0	Lignite (not sampled)							
51.0–54.0	Gray kaolinitic	38.5	42.8	2.0	2.4	13.1	1.2	0.2
54.0–58.0	" "	39.6	41.2	2.6	2.6	13.0	1.0	0.2
58.0–62.0	" "	38.4	40.9	3.8	3.0	12.8	1.1	0.5
62.0–66.0	" "	37.5	41.9	3.8	2.6	13.2	1.0	0.7
66.0–70.0	" "	35.7	39.6	7.2	2.8	13.7	1.0	3.3
70.0–74.0	" "	33.3	40.3	8.4	2.6	13.5	1.9	3.0
74.0–78.0	" "	32.5	36.0	11.6	2.8	15.7	1.4	3.5
78.0–82.0	" "	34.8	35.8	9.7	3.2	15.8	0.7	2.9
82.0–86.8	" "	35.2	35.5	9.1	2.4	16.9	0.9	2.7
86.8–87.8	Tan pisolitic bauxite	52.0	4.1	9.3	3.0	29.6	2.0	6.3
87.8–89.3	No recovery							
89.3–91.3	Tan pisolitic bauxite	51.5	2.9	10.1	3.0	30.4	2.1	6.4
91.3–93.3	" " "	49.1	5.8	11.5	3.1	29.4	1.1	8.6
93.3–95.3	Tan sideritic bauxitic	39.3	16.1	16.1	2.8	24.3	1.4	12.3
95.3–97.3	Gray fragmental sideritic kaolinitic	37.1	37.8	6.5	2.8	15.1	0.7	3.7
97.3–98.3	Gray fragmental sideritic kaolinitic	30.8	33.0	15.4	3.1	16.5	1.2	9.3
98.8–99.3	No recovery							
99.3–103.5	Gray fragmental sideritic kaolinitic	26.1	31.1	21.7	2.4	17.7	1.0	13.3
103.5–106.5	Gray fragmental sideritic kaolinitic	36.7	36.7	8.3	2.2	15.5	0.6	5.0
106.5–109.7	White fragmental kaolinitic	31.9	43.9	4.2	2.6	13.1	5.2	1.1
109.7–113.0	" " "	34.3	39.8	8.1	2.0	14.9	0.9	3.4
113.0–116.7	Soft decomposed syenite	11.9	50.6	3.8	1.2	4.8	27.7	0.6

TABLE IV

CHEMICAL ANALYSES OF TYPICAL HIGH-ALUMINA CLAYS (%)

Sample depth	Description of clays	Al_2O_3	SiO_2	Total Fe as Fe_2O_3	TiO_2	Ignition loss	Insoluble	FeO
57.6–61.6	Gray kaolinitic	38.5	42.9	1.6	2.6	13.5	0.9	0.8
61.6–65.6	" "	39.4	42.3	1.7	3.0	12.7	0.9	0.2
65.6–69.6	" "	39.5	41.9	1.8	2.6	13.2	1.0	0.3
69.6–70.6	Gray carbonaceous (not sampled)							
70.6–76.0	Gray slightly bauxitic	40.6	38.9	1.8	2.8	15.1	0.8	0.2
76.0–78.0	No recovery							
78.0–80.0	Pisolitic bauxite	49.2	3.3	12.1	3.1	30.1	2.2	10.1
80.0–82.0	" "	49.1	3.3	12.4	2.8	30.2	2.2	9.6
82.0–84.0	" "	48.4	5.1	12.3	3.1	29.5	1.6	9.4
84.0–86.0	" "	45.8	8.8	13.5	2.8	28.2	0.9	11.0
86.0–88.0	Tan bauxitic clay	38.1	32.6	7.7	3.0	17.7	0.9	7.3
88.0–90.0	Sideritic bauxitic	25.4	22.8	25.8	3.8	21.6	0.6	23.8
90.0–96.0	White slightly silty	33.0	38.2	9.8	2.6	14.2	2.2	7.3
96.0–100.0	" " "	28.1	31.5	20.2	2.4	16.8	1.0	16.5
100.0–104.0	Red and ocher oxidized Midway	31.9	37.3	12.7	1.6	14.7	1.8	7.9
104.0–107.0	Red and ocher oxidized Midway	29.1	49.1	7.5	2.0	9.5	2.8	0.8
107.0–109.0	Red and ocher oxidized Midway	25.2	53.0	9.2	1.6	9.9	1.1	5.3
109.0–112.0	Dark-gray Midway	23.5	52.8	2.1	1.5	8.7	11.4	0.6

deposit. As a rule, the iron content of a clay deposit is similar to that of the associated bauxite.

III. Chemical Composition

To illustrate the variations in chemical composition of the clays, four sets of analyses of selected cores are given* in Tables I to IV. The cores were chosen as being representative of typical high-alumina clay deposits.

* Chemical analyses by the field laboratory of the Arkansas Bauxite Project, U. S. Bureau of Mines.

In the first set of analyses (Table I), the upper kaolinitic clays and bauxitic clay are 36 feet thick. About 6 feet of bauxite overlies a relatively thin lower clay, which grades into decomposed syenite.

The second set (Table II) shows no bauxite, although 19 feet of bauxitic clay is present. The bauxite-kaolin zone here contains about 50 feet of high-alumina clay.

The third series of analyses (Table III) represents about 70 feet of high-alumina clay, including 6½ feet of bauxite.

The fourth group of analyses (Table IV) represents bauxite-kaolin zone clays that overlie dark-gray to

black clays of Midway age. The oxidized and fresh Midway clays have a relatively high silica content.

IV. Geologic History

The clays of the bauxite-kaolin zone were formed on an ancient land surface. In order to understand their nature, distribution, and extent, it is necessary to know something of the geologic history of the district, and particularly of the physiography during the period in which the clays were formed.

Prior to the formation of the clays, probably in Cretaceous time, the Paleozoic strata of the region were invaded by igneous rocks of the type known as nepheline syenite. The principal constituents of this rock are nepheline and the potassium feldspar, microcline, both of them silicates high in alumina and both, especially the nepheline, easily decomposed by weathering. The moderately metamorphosed Paleozoic rocks were eroded more deeply than the more resistant syenite, which stood forth in a series of rather low hills. During Midway time, a sea advanced over this land surface, and the syenite hills then stood above the sea as islands. Marls and fossiliferous limestones and, later, black silty clays were deposited on the sea floor, lapping on to the flanks of the syenite hills.

Retreat of the Midway sea was followed by a profound weathering of the rocks exposed, which resulted in kaolinization, particularly of the syenite, and in the development of bauxite by removal of silica. The kaolinitic clay and the bauxite developed by the weathering do not form a mantle of even thickness, but lie mainly upon the sides of the valleys draining the syenite hills and upon the surface of the gently dipping Midway clay at the base of the hills. Some of the deposits, therefore, extend along old valleys in the syenite, nearly filling the smaller ones, and others lie at the base of the hills.

Soon after the formation of the high-alumina clays and the bauxite, the region became swampy, and the lignite beds and carbonaceous silty clays of Wilcox age were deposited. Upon these, streams deposited brown sands and clays that buried most of the syenite hills. The thickness of the Wilcox sediments increases away from the higher parts of the buried hills, and these sediments are more than 400 feet thick where they overlie some of the clay deposits.

The uppermost sediments in the area are clays, sands, and gravels of alluvial origin, which in places reach a thickness of more than 100 feet. The Wilcox and younger sediments become thin or disappear where the syenite is close to the present land surface. The shallower deposits of clay and bauxite are thus found in the neighborhood of syenite outcrops, particularly in those areas where the Midway clay lies close to the surface.

V. Availability

The high-alumina clay deposits differ widely in areal extent and in thickness. The tonnage that can profitably be mined from a given deposit depends on how great a thickness of overburden can be stripped economically from the deposit. Assuming arbitrarily that this thickness is 50 feet, the minable deposits range from those that have an areal extent of less than one acre and contain less than 50,000 tons, to those that cover a hundred acres or more and contain over 15 million tons of high-alumina clay.

It seems conservative to estimate that the district as a whole contains at least 100 million tons of ore that is covered by no more than 50 feet of overburden.

As indicated in the discussion of the relations of the high-alumina clays to the bauxite, the clays higher in alumina normally lie near bauxite. Because of this fact, abandoned bauxite pits are a potential source not only of low-grade bauxite but of bauxitic clay and kaolinitic clay already stripped for mining. Although some of the old pits have been filled with the overburden stripped from new areas as the workings were expanded, many of the mined-out pits have been left unfilled.

VI. Conclusion

On account of their size, quality, and accessibility, the deposits of high-alumina clays of Pulaski and Saline counties, Arkansas, warrant further investigation and testing as to their availability for use as refractory clays.

U. S. Department of Interior
Geological Survey
Little Rock, Arkansas

THE SECOND MILE

A Re-Survey—1944

Young men need for their advancement wider sources of information, more varied personal associations, broader stimulation to achievement, and less formal contacts with their seniors than they usually find in their daily jobs. . . . . They can gain much from outside recognition. As men mature they come to value professional rewards—friendships, recognition, responsibility, pride in belonging, evidences of distinction, etc.—no less and often more than money rewards. These are the durable satisfactions of life.

. . . . . .

The engineer needs his profession because of his stake in the advancement of knowledge and technical skill. Who has a larger stake, and who stands to gain more through pooling of effort? The ancients washed occasional nuggets of useful knowledge out of the gravel of common experience by individual placer mining, but science began to get on only when men organized agencies to collect, preserve, and disseminate knowledge and to mine the hidden veins systematically. Otherwise, there would be no profession of engineering. . . . . The general interest and professional advancement alike require that the reservoir of free knowledge, stored by centuries of untrammeled research, be constantly renewed. Few engineers can do much about it alone. Collectively their capacity to advance knowledge is beyond calculation.

Excerpts from "The Second Mile," an address by W. E. Wickenden, revised in 1944; issued by the Engineer's Council for Professional Development, 29 West 39th Street, New York 18, N. Y.

REQUIREMENTS FOR ABILITY IN JOB DIAGNOSIS

[1] Knowledge Beyond That Needed to Master Daily Tasks

[2] Intellectual Attainments in Excess of Technical Practice Demands

[3] Scheduled Study in Collateral Technical Fields

[4] Written Conclusions Based on Recorded Observations and Data

[5] Frequent Convening with Job Diagnosticians in Same and in Allied Work

[6] Contributions to Published Fund of Knowledge

For These Reasons Ceramists Have Their

AMERICAN CERAMIC SOCIETY

Just in case you've eased up... ON YOUR PAY ROLL PLAN

Pause one brief moment. Compare your lot—and that of the men and women in your employ—with the lot of the infantrymen who meet the enemy face to face, who do the hardest fighting, who suffer the most casualties.

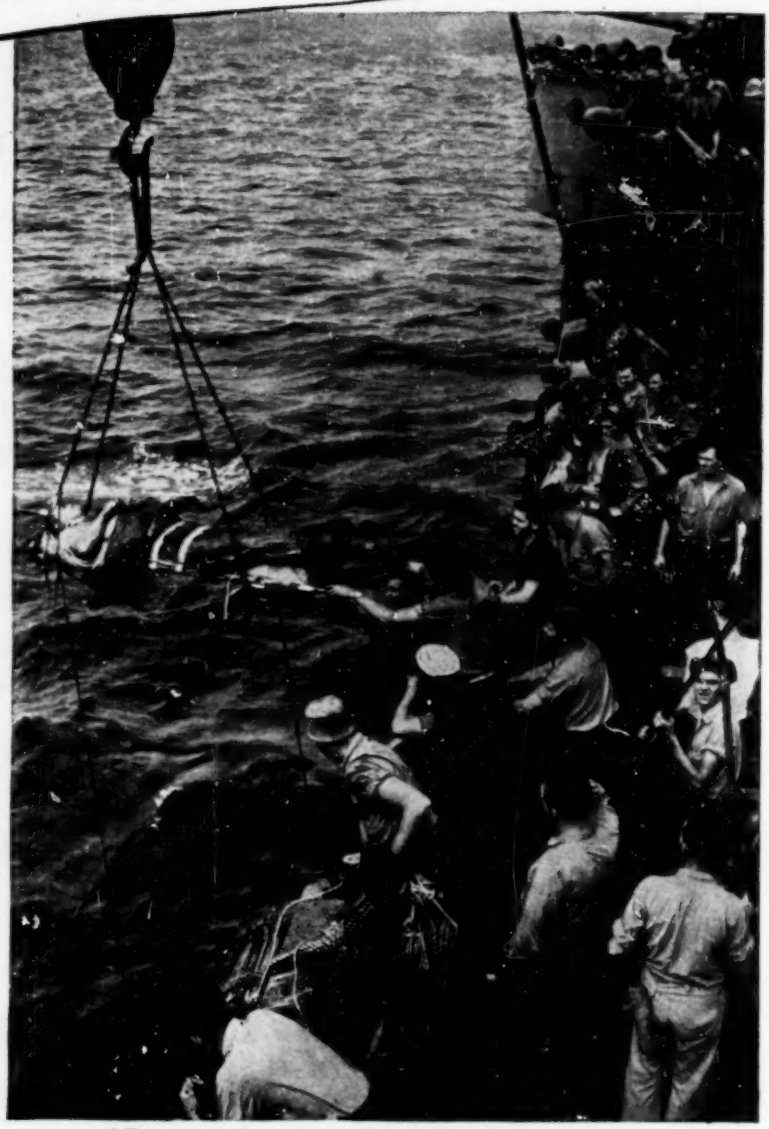
Let the full impact of war's unending grimness swiftly convert any tendency toward complacency into revitalized urgency. Remember—the war is not yet won.

As top management and labor, you've been entrusted with two major responsibilities—steadily maintained production, and steadily maintained War Bond Sales *through your Pay Roll Savings Plan.*

Decide *now* to revitalize your plant's Pay Roll Plan. Have your Bond Committee recheck all employee lists for percentages of participation and individual deductions. Have Team Captains personally contact each old *and new* employee. Raise all percentage figures wherever possible.

Don't underestimate the importance of this task. This marginal group represents *a potential sales increase of 25% to 30% on all Pay Roll Plans!*

Your success will be twofold: A new high in War Bond Sales; and a new high in production. Because a worker with a systematic savings plan has his mind on his work—not on post-war financial worries. He's taking care of the future now. His own. And his Country's future. *Help him!* REVITALIZE YOUR WAR BOND PAY ROLL SAVINGS PLAN.



Official U. S. Coast Guard Photo: The elevator to a Coast Guard-operated transport hospital

Back the Attack!

SELL MORE THAN BEFORE!

The Treasury Department acknowledges with appreciation the publication of this message by

AMERICAN CERAMIC SOCIETY

This is an official U. S. Treasury advertisement—prepared under the auspices of Treasury Department and War Advertising Council.

OFFICIAL PERSONNEL OF DIVISIONS, 1944–1945

	Design	Enamel	Glass	Materials and Equipment	Refractories	Structural Clay Products	White Wares
Trustee	W. A. Weldon	R. L. Fellows	J. S. Gregorius	J. E. Eagle	J. B. Austin	Frederick Heath, Jr.	J. W. Hepplewhite
Chairman	W. A. Weldon	H. D. Carter	K. C. Lyon	J. R. Kauffman	W. R. Kerr	R. L. Stone	J. W. Whittemore
Vice-Chairman	Theodore Lenchner	W. W. Higgins	Louis Navias	J. F. Day	S. M. Swain	E. F. Theobald	R. M. Campbell
Secretary	Myrtle M. French	D. G. Moore	S. R. Scholes	V. J. Koehm	E. E. Callinan	V. W. Boeker	C. M. Lambe, Jr.
Division Nominations	Alice A. Ayars K. E. Smith	F. R. Porter M. J. Bahnsen Karl Kautz	R. A. Miller W. R. Lester L. W. Peterson	J. F. McMahon E. M. Rupp	J. B. Austin C. L. Thompson G. J. Easter	A. P. Potts R. L. Ferguson C. F. Wiseman	J. R. Beam F. C. Henderson R. Russell, Jr.
Papers and Program	C. M. Harder Vincent Broomhall H. L. Moody	W. W. Higgins	Louis Navias	W. E. Dougherty E. W. Emrich J. S. Breitenstein	E. B. Read C. A. Freeman W. S. Debenham B. L. Dorsey	A. C. Jackson H. L. Winburn J. G. Seanor	E. P. McNamara
Membership	W. J. Harr Herbert Tepping G. W. Fichter C. K. Williams	A. I. Andrews J. F. Hunt F. A. Petersen	F. V. Tooley R. R. Shively	V. V. Kelsey	L. C. Hewitt F. E. Lobaugh H. M. Parkhurst E. M. Sarraf	C. F. Tefft R. R. Robinson	A. A. Wells
Standards		R. L. Cook W. N. Harrison R. M. King F. A. Petersen B. W. King, Jr.	Members are Comm. C-14, A.S.T.M.	R. C. Meeker	Members are Comm. C-8, A.S.T.M.	G. R. Robinson	F. P. Hall L. E. Thiess
Research		J. C. Reimers	Alexander Silverman O. G. Burch C. E. Leberknight	R. R. Robinson	E. C. Petrie	G. A. Bole H. C. Plummer	R. Russell, Jr. Glenn Howatt
Classification and Nomenclature	Mrs. J. W. Dixon	G. H. McIntyre E. E. Bryant	E. P. McNamara	J. F. McMahon	C. M. Dodd	E. F. Theobald R. E. Grim	A. S. Watts
Rules	J. P. Thorley	W. A. Deringer O. E. Mulvane	S. R. Scholes	Philip Dressler	S. F. Walton	Howells Fréchette	J. D. Clark
Councillors		D. G. Bennett	R. W. Wampler J. F. Greene	V. V. Kelsey		L. R. Whitaker A. P. Potts	
Exhibitions	Mrs. L. S. Backus		J. E. Frazier				
Industrial Management			C. J. Uhrmann	S. S. Cole	J. L. Crawford	J. C. Peck	
Bibliography	P. E. Cox	J. E. Rosenberg		C. L. Cruikshank			

Officers of Classes

	Institute of Ceramic Engineers	Ceramic Educational Council
Trustee	H. M. Kraner	R. M. Campbell
President	M. F. Beecher	C. M. Dodd
Vice-President	T. A. Klinefelter	A. I. Andrews
Secretary	R. S. Bradley	P. S. Dear

THE AMERICAN CERAMIC SOCIETY TRUSTEES AND OFFICERS FOR 1944–1945

President: E. H. Fritz, Stupakoff Ceramic & Mfg. Co., Latrobe, Pa.
Vice-President: C. Forrest Tefft, The Claycraft Co., Columbus, Ohio
Treasurer: J. D. Sullivan, Battelle Memorial Institute, Columbus 1, Ohio
Secretary-Editor: R. C. Purdy, 2525 North High St., Columbus 2, Ohio
Past-President: C. E. Bales, Ironton Fire Brick Co., Ironton, Ohio
Past-President: L. J. Trostel, General Refractories Co., Baltimore, Md.

TRUSTEES FROM INDUSTRIAL DIVISIONS*

Design: W. A. Weldon, Locke Insulator Corp., Baltimore, Md. (1946)
Enamel: R. L. Fellows, Chicago Vitreous Enamel Product Co., Cicero, Ill. (1946)
Glass: J. S. Gregorius, Pittsburgh Plate Glass Co., Pittsburgh, Pa. (1947)
Materials and Equipment: J. E. Eagle, 6306 20th Ave., Green Meadows, Hyattsville, Md. (1945)
Refractories: J. B. Austin, U. S. Steel Corp., Kearny, N. J. (1946)
Structural Clay Products: Frederick Heath, Jr., Owens-Corning Fiberglas Corp., Toledo, Ohio (1945)
White Wares: J. W. Hepplewhite, Edwin M. Knowles China Co., Newell, W. Va. (1947)
Institute of Ceramic Engineers: H. M. Kraner, Bethlehem Steel Co., Bethlehem, Pa. (1947)
Ceramic Educational Council: R. M. Campbell, New York State College of Ceramics, Alfred, N. Y. (1947)

* Date of expiration of term of office in parentheses.

DIVISION OFFICERS

Design
Chairman: W. A. Weldon, Locke Insulator Corp., Baltimore, Md.
Secretary: Myrtle M. French, Art Institute of Chicago, Chicago, Ill.

Enamel
Chairman: H. D. Carter, Harshaw Chemical Co., Cleveland, Ohio
Secretary: D. G. Moore, National Bureau of Standards, Washington, D. C.

Glass
Chairman: K. C. Lyon, Armstrong Cork Co., Millville, N. J.
Secretary: S. R. Scholes, N. Y. State College of Ceramics, Alfred, N. Y.

Materials and Equipment
Chairman: J. R. Kauffman, Allied Engineering Co., Milltown, N. J.
Secretary: V. J. Roehm, Kentucky Clay Mining Co., Alliance, Ohio

Refractories
Chairman: W. R. Kerr, Armstrong Cork Co., Beaver Falls, Pa.
Secretary: E. E. Callinan, Timken Roller Bearing Co., Timken Steel & Tube Div., Canton, Ohio

Structural Clay Products
Chairman: R. L. Stone, Univ. of North Carolina, Raleigh Unit, Raleigh, N. C.
Secretary: R. L. Ferguson, 730 Stuart Bldg., Lincoln, Nebr.

White Wares
Chairman: J. W. Whittemore, Virginia Polytechnic Institute, Blacksburg, Va.
Secretary: C. M. Lambe, Jr., Univ. of North Carolina, Raleigh Unit, Raleigh, N. C.

OFFICERS OF THE FELLOWS

Dean: R. B. Sosman, U. S. Steel Corp., Kearny, N. J.
Associate Dean: Howells Fréchette, Bureau of Mines, Ottawa, Ontario, Canada.
Secretary-Treasurer: R. M. King, Ohio State University, Columbus, Ohio

INSTITUTE OF CERAMIC ENGINEERS

President: M. F. Beecher, Norton Company, Worcester, Mass.
Vice-President: T. A. Klinefelter, U. S. Bureau of Mines, Tuscaloosa, Ala.
Secretary: R. S. Bradley, A. P. Green Fire Brick Co., Mexico, Mo.

CERAMIC EDUCATIONAL COUNCIL

President: C. M. Dodd, Iowa State College, Ames, Iowa
Vice-President: A. I. Andrews, University of Illinois, Urbana, Ill.
Secretary: Paul S. Dear, Virginia Polytechnic Institute, Blacksburg, Va.

LOCAL SECTIONS

Baltimore-Washington
Chairman: W. R. Lester, Maryland Glass Co., Baltimore, Md.
Secretary: C. B. Shelley, General Refractories Co., Baltimore, Md.

Central Ohio
Chairman: H. J. Orlowski, O.S.U. Engr. Expt. Sta., Columbus, Ohio
Secretary: A. C. Jackson, Claycraft Co., Columbus, Ohio

Chicago
Chairman: Hugo Filippi, Illinois Brick Co., 228 N. LaSalle St., Chicago, Ill.
Secretary: J. J. Svec, Industrial Publications, Inc., 59 E. Van Buren St., Chicago, Ill.

Michigan-Northwestern Ohio
Chairman: J. F. Quirk, A C Spark Plug Co., Flint, Mich.
Secretary: W. V. Blake, Macklin Co., Jackson, Mich.

Northern California
President: W. V. Bragdon, California Faience Co., Berkeley, Calif.
Secretary: P. C. Valentine, Del Monte Properties Co., San Francisco, Calif.

Pacific-Northwest
President: Gordon Adderson, Gladding, McBean & Co., Renton, Wash.
Secretary: K. G. Skinner, Bureau of Mines, Univ. of Washington, Seattle, Wash.

Pittsburgh
Chairman: W. C. Rueckel, Koppers Co., Pittsburgh, Pa.
Secretary: J. W. Jordan, Mellon Institute, Pittsburgh, Pa.

Southern California
Chairman: R. H. Evans, Gladding McBean, & Co. Glendale, Calif.
Secretary: Guy Wurtsbaugh, Pacific Clay Products, Los Angeles, Calif.

St. Louis
Chairman: H. H. Hanna, Pittsburgh Plate Glass Co., Crystal City, Mo.
Secretary: J. H. Ivery, Hydraulic Press Brick Co., St. Louis, Mo.

Upstate New York
Chairman: M. H. Berns, Electro Refractories & Alloys Corp., Buffalo, N. Y.
Secretary: E. E. Kunzman, Titanium Alloy Mfg. Co., Niagara Falls, N. Y.

THE JOURNAL OF THE AMERICAN CERAMIC SOCIETY, AUGUST 1, 1944
Vol. 27, No. 8, pp. 221–252 (1944)